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LETTER TO THE EDITOR

Thermal properties of paratellurite (TeO_2) at low temperatures

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Abstract. Measurements of the heat capacity, C_p, from 0.6 to 15 K can be represented by $C_p = (0.32 \pm 0.02)T^3$ mJ mol^{-1} K^{-1} ($\theta_D^0 = 265 \pm 10$ K) below 10 K. Linear thermal expansivities parallel ($\alpha_\parallel$) and perpendicular ($\alpha_\perp$) to the symmetry axis from 2 to 120 K show marked anisotropy; $\alpha_\perp$ is negative below 10 K (while $\alpha_\parallel$ remains positive) but becomes positive and much larger than $\alpha_\parallel$ above 50 K. The Grüneisen parameter, γ, increases from $\simeq 1$ at 3 K to $+1.4$ at 30 K and is $\simeq 0.9$ at room temperature.

Paratellurite (TeO_2) is of tetragonal structure, related to rutile (e.g. Thomas 1988), and has attracted attention as an electro-optic device material. The elastic constants were measured by Schweppe (1970) and Ohmachi and Uchida (1970) who each showed that the acoustic shear mode propagating in the ⟨110⟩ direction, with polarization along ⟨1$\bar{1}$0⟩ and governed by the elastic modulus, $c' = (c_{11} - c_{12})/2$, had a very low velocity. Paratellurite is also remarkable in that the elastic modulus c_{66} is greater than c_{11}; as a consequence, its fast shear wave propagating in the ⟨100⟩ direction has a higher velocity than the compressive wave. Peercy *et al* (1975) determined the pressure dependence of the acoustic and optic modes of lattice vibration. Earlier, Peercy and Fritz (1973) had shown that a second-order phase transition at 9 kbar is driven by the anomalously slow shear mode governed by c', which is not only weak (small modulus) but also soft (negative pressure coefficient). Ohmachi and Uchida (1970) also gave values for linear thermal expansivity parallel to the c axis ($\alpha_\parallel$) and normal to it ($\alpha_\perp$) from 100 K to room temperature.

In this letter we report expansivity measurements from 2 to 120 K and measurements of the heat capacity, C_p, from 0.6 to 15 K. We calculate values for the Grüneisen parameter, γ, and compare $\gamma(T)$ with the behaviour expected from measurements of the pressure dependence of the elastic moduli.

The samples, which were given to us by Professor Howard Sample of Tufts University, were grown by Itek Corp., Massachusetts. They were three optical-quality rods each about $5 \times 5 \times 21$ mm^3 and with the long axis parallel to ⟨001⟩ or ⟨110⟩. The heat capacity of one rod, of mass 3.0 g, was measured in an adiabatic calorimeter (Collocott 1983) from 0.6 to 15 K. Random errors in the heat capacity are significant

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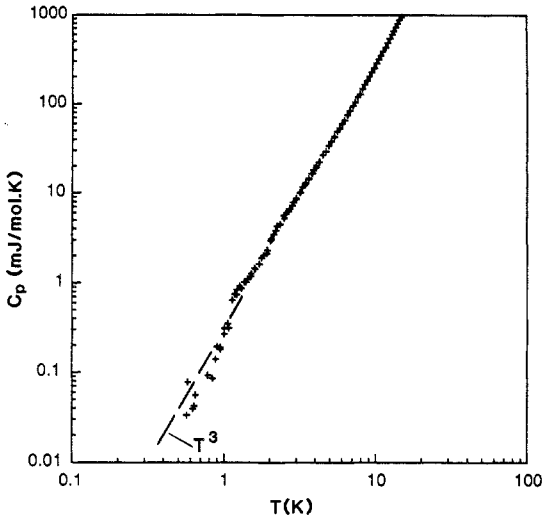

Figure 1. Heat capacity of paratellurite. The dashed curve shows the T^3 behaviour.

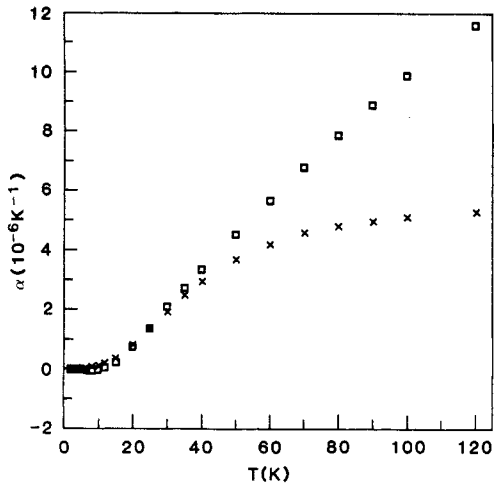

Figure 2. Linear thermal expansion coefficients parallel (×) and perpendicular (□) to the c axis of TeO_2.

below 3 K, where the heat capacity of the addenda increases to more than double that of the small specimen (see figure 1).

The linear thermal expansivities parallel to the symmetry axis (⟨001⟩) and normal to the symmetry axis (⟨110⟩) were measured for two of the rods in a three-terminal capacitance dilatometer (White and Collins 1972) from 1.8 to 125 K and from 273 to 293 K. Expansion values at low temperatures were subject to larger errors than usual due to the small cross-section of the rods, which causes increased sensitivity to vibration. This was particularly true of the measurements perpendicular to the c axis (see figure 2). Repeated measurements of the thermal expansion in this direction revealed a detection limit of ≈0.3 Å (0.03 nm) corresponding to errors of order 0.3×10^{-8} K^{-1} in the coefficient α. Errors in the smoothed values are likely to be $\pm 0.1 \times 10^{-8}$ K^{-1} at the lowest temperatures and of order ±1% at higher temperatures.

Smoothed values of the linear expansion coefficients, $\alpha_{\parallel}$ and $\alpha_{\perp}$, the volume coefficient, $\beta = 2\alpha_{\perp} + \alpha_{\parallel}$, and heat capacity, C_p, are given in table 1. Values of C_p tabulated above 15 K are from Rabinowich *et al* (1978). The Grüneisen parameter, $\gamma = \beta V B_s / C_p$,

Table 1. Thermal expansion coefficients, α, volume expansivity, β, heat capacity, C_p, and Grüneisen parameter, γ, of paratellurite.

T (K)	$\alpha_\parallel$ (10^{-8} K^{-1})	$\alpha_\perp$ (10^{-8} K^{-1})	β (10^{-8} K^{-1})	C_p (J mol^{-1} K^{-1})	γ
2	0.60	−0.4	−0.2	0.0027	−1
3	0.78	−0.8	−0.8	0.0086	−1.2
4	0.96	−1.6	−2.2	0.019	−1.4
5	1.91	−1.9	−1.9	0.036	−0.65
6	2.94	−2.2	−1.5	0.0596	−0.30
8	6.55	−1.9	2.7	0.137	0.25
10	12.3	0.0	12.0	0.270	0.55
12	20.8	5.8	32	0.48	0.83
15	39.4	23.8	87	0.96	1.12
20	83.4	74.5	233	2.20	1.32
25	138	139	416	3.70	1.39
30	195	207	608	5.42	1.39
35	249	273.5	796	7.15	1.38
40	295	336	966	8.9	1.35
50	370	455	1280	12.5	1.27
60	422	565	1552	16.0	1.20
70	460	680	1820	19.5	1.16
80	482	788	2058	23.0	1.11
90	500	890	2280	26.1	1.09
100	512	990	2492	28.9	1.07
120	530	1160	2850	35.8	0.99
283	555	1800	4155	60	0.86

was calculated using room temperature values of molar volume $V = 27$ cm^3 and adiabatic bulk modulus $B_s = 46$ GPa.

The present C_p data below 4 K lead to a low-temperature limiting value for the Debye temperature, θ_D^0, of 265 ± 10 K. Between 10 and 15 K the C_p data correspond to a Debye temperature of ≃275 K which agrees with values obtained by Rabinowich *et al* (1978) at 15 K. Above 15 K $\theta_D(T)$ increases monotonically to ≃370 K at 50 K and 590 K at 200 K. There is no evidence of a significant minimum near $\theta_D^0/15$, such as occurs for most crystals due to the effect of dispersion in the acoustic modes or, less commonly, from low-lying optic modes. In the related rutile crystal TiO_2, Collocott *et al* (1984) observed a deep minimum in $\theta_D(T)$ near 25 K, which was attributed to optic modes of symmetry B_{1u}, B_{1g} and the 'incipient ferroelectric' mode A_{2u}. In MgF_2, which has a similar structure, a less marked minimum in $\theta_D(T)$ at 50 K was attributed to optic modes of B_{1u}, B_{1g} and E_u symmetry plus dispersive contributions. From the room temperature ultrasonic data of Schweppe (1970) and Ohmachi and Uchida (1970) we calculate $\theta_{el}^0 = 232$ K.

Volume extrapolation to helium temperature of the elastic moduli, c_{ij}, measured by Ohmachi and Uchida (1970) leads to a higher value for θ_{el}^0 of ≃240 K. This value is very sensitive to the extrapolation of c_{11} and c_{12} because of the dominant effect of the weak shear modulus $c' \simeq 2.5$ GPa, and suggests that a value closer to the thermal θ_D^0 of 265 K might be obtained from measurements of the elastic moduli at liquid helium temperatures.

Values at 20 °C of $\simeq 20 \times 10^{-6}$ K^{-1} for $\alpha_\perp$ and 6.6×10^{-6} K^{-1} for $\alpha_\parallel$ were reported by Ohmachi and Uchida (1970). These are 10–20% higher than our values. Near 120 K,

Ohmachi and Uchida (1970) obtain values for $\alpha_{\parallel}$ that are comparable with ours, but for $\alpha_{\perp}$ they are much higher. They obtained $\alpha_{\perp} = 17 \times 10^{-6}\,\mathrm{K}^{-1}$ compared with our value of $11.6 \times 10^{-6}\,\mathrm{K}^{-1}$.

The behaviour of $\gamma(T)$ appears to reflect the changing dominance of the various lattice modes. At room temperature, the value of $\gamma \simeq 0.9$ is consistent with the average over individual γ_i for all the modes, given that we have only evidence of γ_i for acoustic modes in the long-wave ($q \rightarrow 0$) limit (see Peercy *et al* 1975). Below 100 K, $\gamma(T)$ increases due presumably to the influence of the optic mode of B_1 symmetry which Peercy *et al* (1975) found to have a frequency of 62 cm^{-1} and $\gamma_i = 1.3$. At much lower temperatures the influence of the low-lying shear mode, c', becomes dominant. Its pressure derivative (Peercy *et al* 1975, Antonenko *et al* 1979) leads to $\gamma_i = -1.4$ for this mode and this leads to an averaged Grüneisen parameter of about -1 as $T \rightarrow 0$ K.

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