The elastic constants of IV–VI compound alloys

The technological importance of IV–VI compounds as detectors of infra-red radiation has motivated extensive studies of these materials. Applications are not limited to the pure compounds – their alloys also find use. Thus SnTe–PbTe and SnSe–PbSe solid solutions have been used to make photoconductive and photovoltaic detectors for wavelengths as long as 20 μm and *p-n* junction injection lasers in the far infra-red [1, 2]. The IV–VI compounds are mixed covalent-ionic semiconductors with unusually high dielectric constants [3, 4] and can exhibit lattice instability in the form of a soft zone centre TO phonon mode [5–7]. This optic mode softening can have pronounced effects on the elastic and anelastic properties, for instance in the $Ge_xSn_{1-x}Te$ alloys in the vicinity of the ferroelectric fcc–fcr phase transition temperature the elastic constants decrease markedly and there is an attenuation peak [8–10]. Ultrasonic wave measurements have been made in the SnTe–PbTe alloys to see whether either band inversion and band crossover effects, which occur in these alloys [11], or any mode softening influence the elastic properties. The results obtained provide information basic to studies of lattice dynamics and interatomic binding forces in the IV–VI compound alloys.

Ultrasonic wave velocity measurements have been made at 15 MHz to an accuracy of better than 1 part in 10^3 by the pulse echo overlap technique [12] in the [1 1 0] direction of Bridgman grown, single crystals of the rock salt structure PbTe alloys with SnTe and CdTe. Room temperature results and the calculated elastic constants C_{ij} and S_{ij} are presented in the table. As the SnTe content is increased, the ultrasonic velocities and C_{11} and C_{44} increase somewhat but much less than that suggested by the published data on $Pb_{0.5}Sn_{0.5}Te$ [14] which gives substantially larger values for

$$V_L \left(= \left\{\frac{1}{2\rho}(C_{11}+C_{12}+2C_{44})\right\}^{1/2}\right)$$

$$\text{and } V_s\ (q /\!/ [1\,\bar{1}\,0]) \left(= \left\{\frac{1}{2\rho}(C_{11}-C_{12})\right\}^{1/2}\right)$$

for two of the waves propagated down the [1 1 0] direction than those found here for $Pb_{0.47}Sn_{0.53}Te$. Particular care has been taken to check the measurements and establish this discrepancy. Unlike the data reported in this note, the results of Pratt and Das [14] for $Pb_{0.5}Sn_{0.5}Te$ indicate that C_{11} is much larger in the alloy than in the parent compounds and that the technical moduli such as bulk modulus, compressibility and Young's modulus are completely different in the alloy from those of PbTe or SnTe. The marked difference between the moduli of $Pb_{0.5}Sn_{0.5}Te$ [14] and $Pb_{0.47}Sn_{0.53}Te$ (this work) ought not to arise from any substantial difference in the hole contributions to the elastic constants because (i) the hole concentrations of the two specimens are similar and (ii) the elastic constant expected to be affected by carriers in the L-point pockets is C_{44} rather than C_{11}.

The value of S_{12} in the compounds and alloys is very small. One interesting ramification of this is that the Poisson ratio γ_{ij} $(= -S_{jjii}/S_{iiii})$ is particularly small for a stress applied in a ⟨1 0 0⟩ direction. The Poisson ratio γ'_{ij} for an arbitrary set of axes has been calculated from S'_{iijj}/S'_{iiii} using the tensor transformation law

$$S'_{ijkl} = a_{im}a_{jn}a_{kp}a_{lq}S_{mnpq} \qquad (1)$$

to obtain the primed compliance from the unprimed ones [15, 16]. Plots of the angular dependence of the Poisson ratio of $Pb_{0.47}Sn_{0.53}Te$ for selected planes superimposed on a standard projection are shown in Fig. 1; the centre of the plot coincides with the point on the standard projection which represents the plane perpendicular.

Recently, it has been shown for p-type SnTe that C_{44} is sensitive to the hole concentration whereas $\frac{1}{2}(C_{11}-C_{12})$ is not, a finding consistent with the valence band pockets being sited near the L-points of the Brillouin zone [17]: the hole contribution to C_{44} in a multivalley semiconductor with ν valleys given by

$$\Delta C_{44} = \frac{-4\pi\nu}{9h^3}E_u^2(2m*)^{3/2}(kT)^{1/2}\left[F_{-1/2}(\eta) + \frac{6kT}{E_g}F_{1/2}(\eta)\right] \qquad (2)$$

is much enhanced in the non-ellipsoidal, non-

TABLE I The elastic constants of PbTe and SnTe and their alloys

Reference	PbTe [13]	$Pb_{0.97}Cd_{0.03}Te$	$Pb_{0.71}Sn_{0.29}Te$	$Pb_{0.50}Sn_{0.50}Te$ [14]	$Pb_{0.47}Sn_{0.53}Te$	$Pb_{0.05}Sn_{0.95}Te$	SnTe
Lattice parameter a_0 (Å)	6.461	–	6.418	6.387	6.382	6.320	6.304
Density ρ (g cm^{-3})	8.25	8.18	7.77	7.14	7.35	6.60	6.51
N/V (atoms cm^{-3}) × 10^{22}	2.966	2.968	3.026	3.070	3.075	3.169	3.183
θ_D Debye temperature (K) (calculated from room temperature C_{ij})	159.7	161.6	164.7	181.7	180.0	187.1	170.5
Velocities of wave propagated down the [1 1 0] direction (cm sec^{-1}) × 10^5							
v (longitudinal)	(2.95)	2.84	2.93	4.08	3.29	3.32	3.171
v (shear $q /\!/ [0\,0\,1]$)	(1.28)	1.29	1.30	1.344	1.38	1.47	1.22
v (shear $q /\!/ [1\,\bar{1}\,0]$)	(2.47)	2.33	2.60	3.24	2.66	2.79	2.869
Elastic stiffness constants (dyn cm^{-2}) × 10^{11}							
C_{11}	10.80	9.64	10.6	18.10	11.73	11.0	10.93
C_{12}	0.77	0.79	0.14	0.31	1.34	0.69	0.21
C_{44}	1.34	1.36	1.31	1.30	1.41	1.43	0.969
Elastic compliance constants (cm^2 dyn^{-1}) × 10^{-12}							
S_{11}	0.935	1.05	0.941	0.582	0.873	0.917	0.916
S_{12}	−0.062	−0.080	−0.012	−0.085	−0.089	−0.054	−0.017
S_{44}	7.46	7.35	7.62	7.690	7.69	6.990	10.3
Linear compressibility (cm^2 dyn^{-1}) × 10^{-12}	0.810	0.891	0.917	0.412	0.694	0.808	0.881
Volume compressibility (cm^2 dyn) × 10^{-12}	2.43	2.67	2.75	1.24	2.08	2.43	2.64
Bulk modulus (dyn cm^{-2}) × 10^{12}	0.411	0.374	0.364	0.810	0.480	0.412	0.378
Young's modulus (dyn cm^{-2}) × 10^{12}							
[1 0 0] in (0 0 1) plane	1.07	0.95	1.06	1.718	1.14	1.09	1.09
[1 1 0] in (0 0 1) plane	0.436	0.43	0.423	0.461	0.462	0.459	0.330
[1 1 1] in (1 1 0) plane	0.363	0.378	0.352	0.370	0.402	0.385	0.281
Hole concentration (cm^{-3})	3×10^{18}	–	5×10^{19}	6.8×10^{19}	6.6×10^{19}	6.7×10^{19}	4.5×10^{20}

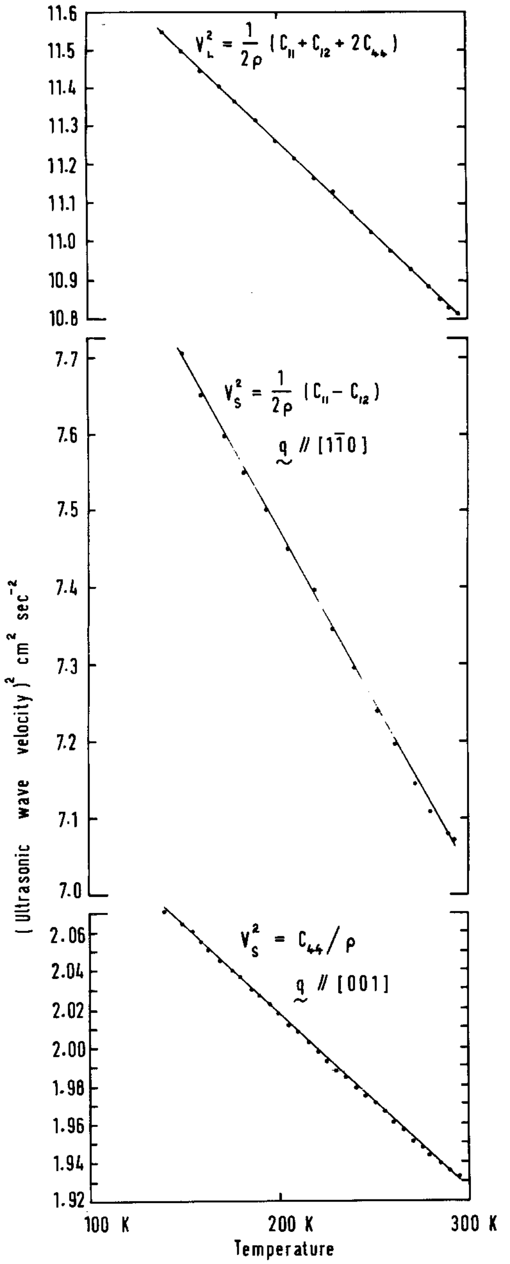

Figure 1 The temperature dependences of the square of the velocity of each of the three ultrasonic modes which propagate down the [1 1 0] direction in $Pb_{0.47}Sn_{0.53}Te$ alloy single crystals. There is no evidence for a change in slope of these elastic constants in the $L_6^+ \rightarrow L_6^-$ band crossover region.

parabolic (NENP) model [17, 18]. This enhancement should also accrue in C_{44} for the $Pb_{1-x}Sn_xTe$ alloys, especially in the region of the $L_6^+ \rightarrow L_6^-$ band crossover when the direct L-point band gap E_g is small [1, 11] and the NENP nature is consequently more pronounced. Thus there should be significant hole contributions to C_{44} in these alloys; estimates of this, using Equation 2 and taking the valence band deformation potential E_u as that of SnTe:7.8 eV [17], show that C_{44} is about 10% smaller in each of alloys listed in the table than it would be in undoped crystals. The effect of doping SnTe itself with 4.5×10^{20} holes cm^{-3} is to reduce C_{44} from 1.4×10^{11} to 0.969×10^{11} dyn cm^{-2} [17]. Pratt and Das [14] observed a change in slope at about 210 K in the temperature dependence of C_{44} in $Pb_{0.5}Sn_{0.5}Te$ which they attributed to the effect of the $L_6^+ \rightarrow L_6^-$ band crossover. The temperature dependences of the ultrasonic wave velocities have been measured in the present work.

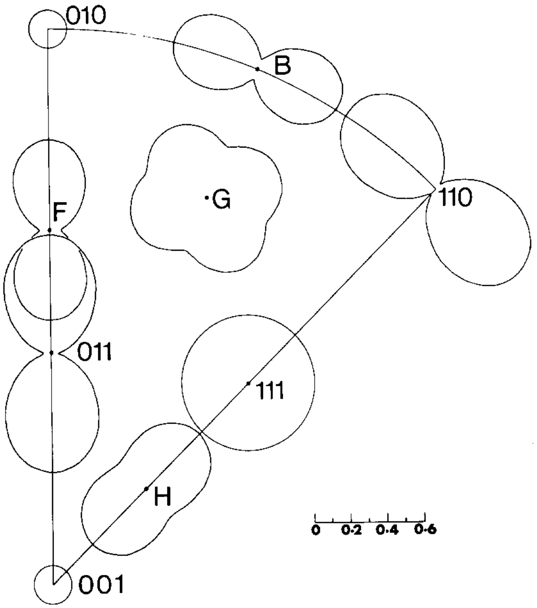

Figure 2 The directional dependence of the Poisson ratio in $Pb_{0.47}Sn_{0.53}Te$. The diagrams are shown superimposed on to a stereographic projection on the (0 0 1) plane; the [0 0 1] axis comes out of the plane of the paper. Direction cosines of those poles, which are not marked with Miller indices are: B(0.383, 0.924, 0); F(0, 0.924, 0.383); G(0.360, 0.868, 0.342); H(0.333, 0.333, 0.882).

Fig. 2 illustrates a typical result – that for $Pb_{0.47}Sn_{0.53}Te$, the closest composition studied here to $Pb_{0.5}Sn_{0.5}Te$. The temperature dependences do not show any change of slope for C_{44} for this or any of the other alloys. Although the pulse echo overlap technique is a very sensitive way of measuring the temperature dependence of velocity, the $L_6^+ \rightarrow L_6^-$ band crossover has not produced any measurable effect on C_{44}. An anomalous change in the temperature dependence of C_{44} at the $L_6^+ \to L_6^-$ band crossover could arise either from an appreciable change in either (i) carrier concentration or (ii) the deformation potential characteristics of the bands. However, measurements of Hall coefficient as a function of temperature do not reveal any appreciable change in the carrier concentration at the $L_6^+ \to L_6^-$ crossover. As the L_6^+ and L_6^- bands have mirror symmetry, parameters in the two bands should be of similar magnitude – the deformation potential constants should be similar for the two bands. Theoretical calculations show this to be so for SnTe [19]. The slope of C_{44} before and after the $L_6^+ \to L_6^-$ crossover depends upon E_u^2; thus the present experimental results suggest that the deformation potentials for the L_6^+ and L_6^- bands are almost equal for $Pb_{0.47}Sn_{0.53}Te$.

Furthermore, in general the elastic constants of the $Pb_xSn_{1-x}Te$ alloys do not depend markedly upon composition and do not evidence any marked degree of acoustic phonon mode softening even for alloys with composition in the band crossover region.

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Growth of hematite single crystals by chemical transport with $TeCl_4$

Ferric oxide is the main component of ferrite materials which have various applications. For this reason, the study of the methods and conditions of preparation of α-Fe_2O_3 single crystals is of considerable interest.

In a previous paper [1] it was established by means of thermodynamic considerations that $TeCl_4$ should be one of the best carriers in the chemical transport of hematite. In this case, the following reactions could take place when working in a closed system:

$$Fe_2O_{3(s)} + 1.5TeCl_{4(g)} = 2FeCl_{3(g)} + 1.5TeO_{2(g)}, \quad (1)$$

$$TeCl_{4(g)} = TeCl_{2(g)} + Cl_{2(g)}, \quad (2)$$

$$TeO_{2(g)} = 0.5Te_{2(g)} + O_{2(g)}, \quad (3)$$

$$TeO_{2(g)} = TeO_{(g)} + 0.50_{2(g)}, \quad (4)$$