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Ultrasonic studies of thulium monochalcogenides

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The ultrasonic studies have been made in a group of materials like thulium monochalcogenides Tm*X* (*X* = S, Se and Te) which are very important because TmS behaves like a metallic crystal, TmSe is intermetallic and TmTe is a semiconductor. Thus, the ultrasonic study will give a clear picture of ultrasonic attenuation in these substances. Morse potential has been used for the evaluation of second order elastic constants (SOEC) and third order elastic constants (TOEC) for TmS and TmTe which is the most appropriate method. However, Coulomb and Born Mayer potentials are the most appropriate for evaluation of SOEC and TOEC in semiconductors. Then, the Mason's approach has been used for the evaluation of ultrasonic attenuation.

Keywords: Ultrasonics, Coulomb potential, Born Mayer potential, Morse potential, Elastic constants, Monochalcogenides
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1 Introduction

Ultrasonic studies have been made extensively, both theoretically and experimentally in solids, liquids and liquid crystals[1-4]. In the present paper, the ultrasonic attenuation has been made in TmS, which behaves like a metallic crystal, TmSe as intermetallic crystal and TmTe as a semiconductor crystal[5]. There are several causes of ultrasonic attenuation in solids[6] for e.g. the phonon-phonon (p-p) interaction above 100 K. Several methods are known for the evaluation of ultrasonic attenuations theoretically, but the most extensively used one is the approach of Mason[6] using second order elastic constants (SOEC) and third order elastic constants (TOEC). The first principle methods are available for the evaluation of SOEC and TOEC, which are more accurate and reliable. Morse potential[7] is the appropriate one for studying the physical properties of metallic crystals. In the present work, Morse potential has been used to obtain SOEC and TOEC for TmS and TmSe.The Coulomb and Born-Mayer potentials[8] have been used to obtain SOEC and TOEC for TmTe at 0 K and in the temperature[9,10] range 100-500 K. Finally, the ultrasonic attenuations are evaluated. The evaluations are quite extensive and have been made using program in basic language.

2 Theory

2.1 SOEC and TOEC by Morse potential

The interaction energy according to Morse potential is given by[7]

$$\phi(r_{\mathrm{ij}}) = D[e^{-2\alpha(r_{\mathrm{ij}}-r_0)} - 2e^{-\alpha(r_{\mathrm{ij}}-r_0)}] \qquad \ldots (1)$$

where, r_i is the distance of the ith atom from origin (0,0,0), D the dissociation energy, r_o the equilibrium distance of approach of the two and α is a parameter related to hardness of potential with dimension of reciprocal distance. The Morse parameters are obtained from the following Eqs:

$$\mathrm{d}\phi/\mathrm{d}u = 0 \text{ at } a = a_o \qquad \ldots(2)$$

Bulk modulus (B) is written as:

$$B = (a_o/9V_o)\,(\mathrm{d}^2\phi/\mathrm{d}a^2)_{a=ao} \qquad \ldots(3)$$

$$\text{and } r_j = [m_j^2 + n_j^2 + l_j^2]^{1/2}\, a = M_j\, a \qquad \ldots(4)$$

where: m_j, n_j and l_j are the position coordinates of any atom in terms of half the lattice parameter. The expression for SOEC (C_{11}) is as follows:

$$C_{11} = \frac{2Da^2\alpha^2\beta^2}{V_o}\sum\frac{m_j e^{-2\alpha a M_j}}{M_j} - \frac{2Da^2\alpha^2\beta}{V_o}\sum\frac{m_j^4 e^{-\alpha a M_j}}{M_j^2} + \frac{Da\alpha\beta}{V_o}\sum\frac{m_j^4 e^{-2\alpha a M_j}}{M_j^3} \times \frac{Da\alpha\beta}{V_o}\sum\frac{m_j^4 e^{-\alpha a M_j}}{M_j^3} \qquad \ldots(5)$$

where $\beta = e^{\alpha r_o}$.

The expression for C_{12} is obtained by replacing m_j^4 by $m_j^2\, n_j^2$ in Eq. (5) above and V_o the volume of the f c c lattice.

The expression for TOEC (C_{111}) is as follows:

$$C_{111}=-\frac{4Da^2\alpha^2\beta^2}{V_o}\sum\frac{m_j^6 e^{-2a\alpha M_j}}{M_j^3} - \frac{6Da^2\alpha^2\beta}{V_o}\sum\frac{m_j^8\, e^{-2\alpha a M_j}}{M_j^3} - \frac{3Da\alpha\beta^2}{V_o}\sum\frac{m_j^6\, e^{-2\alpha a M_j}}{M_j^5} + \frac{Da^3\alpha^3\beta}{V_o}\sum\frac{m_j^6 e^{-\alpha a M_j}}{M_j^3} + \frac{3Da^2\alpha^2\beta}{V_o}\sum\frac{m_j^6\, e^{-2a\alpha M_j}}{M_j^4} + \sum\frac{m_j^6 e^{-\alpha a M_j}}{M_j^5} \quad \ldots(6)$$

The expression for C_{112} ($=C_{166}$) is obtained by replacing m_j^6 by $m_j^4\, n_j^2$ in all the summations in Eq.(6). Also, the expression for C_{123} which is equal to $C_{456} = C_{144}$ is obtained by replacing m_j^6 by $m_j^2\, n_j^2\, l_j^2$ in all summations in Eq. (6).

2.2 SOEC and TOEC by Coulomb and Born-Mayer potentials[8]

The potential used for evaluation of SOEC and TOEC is:

$$\phi_c=(z^2 e^2/r) \text{ and } \phi_r = A \exp(-r/\rho) \quad \ldots(7)$$

ϕ_c is the electrostatic potential and ϕ_r the repulsive potential, r the nearest neighbour distance and ρ is the hardness parameter[11] used by us for SOEC and TOEC and not repeated here.

2.3 Temperature dependence of SOEC and TOEC

According to the lattice dynamics developed by Leibfried[10], lattice energy changes with temperature, hence adding its vibrational energy contribution to elastic constants at absolute zero one gets C_{ij} and C_{ijk} (SOEC and TOEC) at the required temperature.

$$C_{ij}(T) = C_{ij}^{o} + a_{ij}(T) \quad \ldots(8)$$

$$C_{ijk}(\mathrm{T}) = C_{ijk}^{o} + a_{ijk}(T) \quad \ldots(9)$$

where the superscript has been used to denote SOEC and TOEC at absolute zero. The a_{ij} and a_{ijk} are vibrational contributions and functions of various G's, which are functions of r_o and ρ_o and presented in our earlier paper[11].

2.4 Ultrasonic attenuation due to phonon-phonon interaction

Akhiezer[12,13] was the first to propose the phonon viscosity mechanism for the ultrasonic attenuation due to p-p interaction. Mason[6] used Grüneisen constants in Akhiezer region ($\omega\, \tau_{th} <<1$) and is given by:

$$(\alpha/f^2)_l = \frac{(2\Pi)^2\tau_{th}E_o\Gamma_l}{6dv_l^3} \quad \ldots(10)$$

$(\alpha/f^2)_l$ is for longitudinal wave, Γ the non-linearity constant, d the density, v_l the longitudinal velocity and τ_{th} the thermal relaxation time. Similarly, l is replaced by s for shear waves.

Mason's non-linearity constant Γ is given by:

$$\Gamma = 9 <\gamma_{ij}^2> - 3\, C_v \mathrm{T} < \gamma_{ij} >^2/E_o \quad \ldots(11)$$

$< \gamma_i^j >$ and $< \gamma_i^j >^2$ are the average Grüneisen parameter and square average Grüneisen numbers respectively, which are obtained using Grüneisen tables[6] along <100> and other direction of propagation and are functions of SOEC and TOEC, C_v is the specific heat per unit volume, T is the absolute temperature, E_o is the energy of the crystal. All the constants are taken from AIP handbook[14].

Equations (1-4) are used for the evaluation of Morse parameters D, α and r_o using experimental values of lattice parameter[5]. For bulk modulus the elastic constants C_{12} and C_{44} are evaluated by Coulomb and Born-Mayer potentials and then the bulk modulus[15] and the cohesive energy are evaluated as given in literature[16]. These values of D, α and r_o are then used to evaluate SOEC and TOEC at absolute zero using Eqs (5) and (6) by Morse potential. SOEC and TOEC at absolute zero are also calculated for TmTe by Coulomb and Born-Mayer potentials[8]. Then the temperature dependence of SOEC and TOEC[11] and finally the ultrasonic attenuation is obtained from Eq. (10).

3 Results and Discussion

Morse parameters D, α and r_o for TmS and TmSe are presented in Table 1. For TmTe the nearest neighbour distance and hardness parameter are 4.39Å and 0.313Å. Temperature dependence of elastic constants are given in Table 2. The variations of elastic constants with temperature are as expected and

Table 1—Values of Morse parameters

Material	α [in Å^{-1}]	R_0 [in Å]	D [in10^{-20} Joule]
TmS	0.860	3.87 0	3.906
TmSe	0.585	5.333	2.236

Table 2—Values of the SOEC and TOEC in TmS, TmSe and TmTe as a function of temperature (all in 10^{10} N m^{-2})

Material	T(K)	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	C_{456}
TmS	100	3.54	2.17	2.37	–21.8	–14.1	1.46	1.79	–15.5	1.79
	200	3.75	2.20	2.37	–24.9	–14.9	0.96	1.79	–15.5	1.79
	300	3.96	2.24	2.38	–27.3	–15.4	0.48	1.79	–15.6	1.79
	400	4.00	2.28	2.38	–30.0	–15.8	0.24	1.79	–15.6	1.79
	500	4.40	3.20	2.39	–33.3	–16.3	0.08	1.79	–15.7	1.79
TmSe	100	0.47	0.29	0.40	–3.54	–2.37	0.27	0.67	–2.96	0.68
	200	0.68	0.29	0.41	–6.06	–2.83	0.21	0.67	–2.99	0.68
	300	0.89	0.27	0.41	–8.25	–3.07	0.67	0.67	–3.03	0.68
	400	1.10	0.24	0.42	–10.40	–3.25	1.10	0.67	–3.07	0.68
	500	1.33	.022	0.42	–12.80	–3.42	1.60	0.67	–3.12	0.68
TmTe	100	7.09	0.84	0.89	–149.9	–3.06	1.21	1.68	–3.35	1.69
	200	7.19	0.79	0.90	–150.5	–2.77	0.73	1.69	–3.36	1.69
	300	7.30	0.74	0.90	–151.3	–2.48	0.25	1.69	–3.36	1.69
	400	7.41	0.69	0.91	–152.1	–2.19	–0.23	1.70	–3.36	1.69
	500	7.53	0.64	0.91	–152.9	–1.90	–0.71	1.70	–3.37	1.69

Table 3—Ultrasonic attenuation (α/f^2) in Tms, TmSe and TmTe along $<100>_l$, $<100>_S$ and due to thermo-elastic relaxation

Material	Temperature (K)	$<100>_l$ 10^{-17} (Nps^{2}cm^{-1})	$<100>_S$ 10^{-17}(Nps^2 cm^{-1})	$(\alpha/f^2)_{th}$ (Nps^{2}cm^{-1})
TmS	100	0.49	0.03	0.60×10^{-21}
	200	0.58	0.18	0.61×10^{-21}
	300	0.75	0.41	0.73×10^{-21}
	400	1.16	0.67	0.82×10^{-21}
	500	8.18	4.57	0.92×10^{-21}
TmSe	100	1.90	0.87	0.92×10^{-20}
	200	4.60	2.80	0.85×10^{-20}
	300	8.40	5.47	0.67×10^{-20}
	400	10.2	7.60	0.51×10^{-20}
	500	11.6	11.6	0.37×10^{-20}
TmTe	100	0.33	0.05	0.18×10^{-28}
	200	0.45	0.45	0.16×10^{-28}
	300	0.90	0.90	0.14×10^{-28}
	400	1.81	1.70	0.12×10^{-28}
	500	2.00	1.90	0.11×10^{-28}

are of the same order of magnitude as for other substances. The signs of TOEC viz C_{111}, C_{112} and C_{166} are negative as obtained by the two potentials, as reported in several cases[17,18] . Values of C_{123} are positive and decrease very rapidly and then the values are negative as observed in earlier cases[19]. The ultrasonic attenuation due to p-p interaction and its temperature dependence is as expected and is of the order of 10^{-17} Nps^{2}cm^{-1}. The attenuation due to thermoelastic relaxation is of the order of 10^{-20} Nps^{2}cm^{-1} (Table 3). However, the ultrasonic attenuation for TmTe is of the order of 10^{-28} Nps^{2}cm^{-1} which is due to thermoelastic relaxation. The thermal conductivity of TmTe is high and one may conclude that by evaluation of ultrasonic attenuation one can assure if the substance is a semiconductor or not. The comparison with earlier values[19]shows that the values are of the same order of magnitude.

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