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Elasticity of the $Sm_{1-x}Y_xS$ alloy Based on Ultrasonic Measurements

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Abstract. The elastic moduli, sound velocities, Grüneisen parameter, Poisson's ratios and brittleness-plasticity criterion ratios are studied for the $Sm_{1-x}Y_xS$ alloys. Their dependence on the concentration of alloy components including a valence transition from semiconductors into the metal phase is presented. Auxeticity (negative Poisson's ratio) is found for some concentrations.

1. Introduction

In recent years there has been increasing interest observed in studies of materials with negative Poisson's ratio ($\sigma < 0$) which are called "auxetics" [1]. Scientists have studied mechanisms and have established criteria of negative Poisson's ratios appearance in isotropic and anisotropic solids [1,2]. The extreme values $\sigma = 0.5$ and $\sigma = -1$ for ideal elastic continuous media were analyzed from the point of view of physical acoustics as its methods were widely used in experimental studies of elastic properties of various materials [3]. Previously we completed a brief analysis of sound velocities relations in the context of limit values of Poisson's ratios for 94 elastically isotropic elements and compounds including four auxetics [4]. In a number of cases there was a disagreement in the values of Poisson's ratios for one and the same substance when calculating with various relations of sound velocities although the initial formulas of elasticity theory for σ through elastic moduli were equivalent. We used the data for elastic parameters of polycrystals obtained from rigidity constants in accordance with constants of monocrystals in Voigt-Royce-Hill approximation [5].

In this work we study the interrelation of sound velocities and Poisson's ratios relations by the example of only one system $Sm_{1-x}Y_xS$ but in more detail than in [4]. The choice of this object is determined by the fact that constant c_{12} according to experimental results [6] takes positive or negative values depending on yttrium concentration in samarium sulfide. The given fact allows one for more unambiguous treatment of the limits of sound velocities relations when the hybrid system transits into the auxetic state. Besides, $\sigma < 0$ in $Sm_{1-x}Y_xS$ is registered near valence transition $Sm^{2+} \rightarrow Sm^{3+}$ [7] and study of materials with the intermediate valence in relation to their simultaneous demonstration of anomalous properties is of special interest.

2. Calculations

The known formulas for the Poisson's ratios of isotropic bodies [3, 8] could be applied to approximate the formulas for σ expressed through the sound velocities:

$$\sigma_x = \frac{x^2 - 2}{2x^2 - 2}, \quad x = \frac{\upsilon_L}{\upsilon_t} \tag{1}$$

$$\sigma_y = 0.5y^2 - 1, \quad y = \frac{\upsilon_\ell}{\upsilon_t} \tag{2}$$

$$\sigma_{xy} = 0.5 - \frac{y^2}{6x^2 - 8} \tag{3}$$

$$\sigma_{z_{1,2}} = \frac{-\left(z^2 - 1\right) \pm \sqrt{\left(z^2 - 1\right)^2 + 8z^2\left(z^2 - 1\right)}}{4z^2}, \; z = \frac{\upsilon_L}{\upsilon_\ell}, \tag{4}$$

where υ_t – velocity of propagation for transverse elastic waves, υ_ℓ – velocity of longitudinal waves propagation in the plug, υ_L – velocity of propagation longitudinal elastic waves.

However, no experimental values are known for elastic moduli of $Sm_{1-x}Y_xS$ polycrystals and sound velocities in them. Therefore in the present work we provide calculations of bulk and shear moduli based on rigidity constants c_{11}, c_{12} and c_{44} of this system cubic monocrystals measured by the pulse ultrasonic method [6]. When establishing the given moduli we applied the approximations of Voigt (B_V, G_V), Royce (B_R, G_R), Voigt-Royce-Hill (B_{VRH}, G_{VRH}) [5], G. Peresada (G_{Per}) [9], K.S. Alexandrov (G_{Al}) [10]. Poisson's ratios along the specific crystallographic directions, $\sigma_{<hk\ell>}$ were calculated according to the formulas presented in the references [2, 6].

Velocities of purely longitudinal and traverse waves propagation for isotropic elastic bodies and in three specific directions of cubic monocrystals of hybrid system $Sm_{1-x}Y_xS$ were found through the known relations of elasticity theory and physical acoustics [5, 8, 11, 12].

Grüneisen parameter γ, a nonharmonic measure of interatomic oscillations and non-linearity of interatomic interrelation forces, was calculated according to the previously established formula [12]:

$$\gamma = \frac{3}{2}\left(\frac{3\upsilon_L^2 - 4\upsilon_t^2}{\upsilon_L^2 + 2\upsilon_t^2}\right). \tag{5}$$

3. Results and their discussion

Changes of velocities of elastic waves propagation in crystallographic directions <100>, <110> and <111> of cubic monocrystals $Sm_{1-x}Y_xS$ depending on their composition are presented in Figure 1 (a, b, c). The obtained data provide us with a number of basic conclusions: functions $\upsilon_L(x)$, $\upsilon_t(x)$ are linear in both phases of the studied system; dependence $\upsilon_\ell(x)$ is linear only in semiconductor phase $Sm_{1-x}Y_xS$; with the growth of yttrium concentration at the initial stage ($0 < x \le x_c$, where x_c – critical concentration) velocities of traverse waves propagation decrease and those of longitudinal waves increase; acoustic anisotropy is qualitatively equal for longitudinal waves ($\upsilon_{L\langle 100\rangle} > \upsilon_{L\langle 110\rangle} > \upsilon_{L\langle 111\rangle}$, $\upsilon_{\ell\langle 100\rangle} > \upsilon_{\ell\langle 110\rangle} > \upsilon_{\ell\langle 111\rangle}$) and is different for traverse waves ($\upsilon_{t_2\langle 110\rangle} > \upsilon_{t\langle 111\rangle} > \upsilon_{t\langle 100\rangle} = \upsilon_{t_1\langle 110\rangle}$); at the isostructural transition all sound velocities change abruptly (in a discontinuous way) but differently in terms of quality and quantity: velocities of longitudinal waves decrease, velocities of traverse waves increase. The data on the mentioned fact are given in Table 1 (here "+"corresponds to the discountinuous growth of sound velocity at the alloy transition from the semiconductor phase into the metallic one and "–"corresponds to the discountinuous decrease).

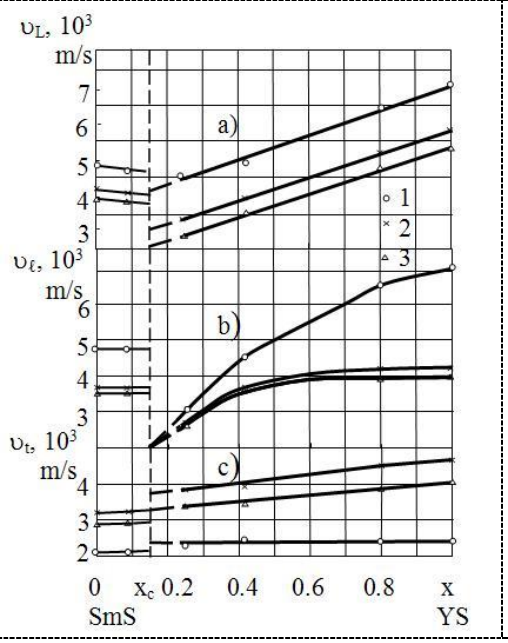

Figure 1. Concentration dependence of propagation velocities for longitudinal (υ_L, υ_ℓ) and traverse (υ_t) elastic waves in specific directions of $Sm_{1-x}Y_xS$ monocrystals.

1 – <100>, 2 – <110>, 3 – <111>, x_c – critical concentration, $\upsilon_{t_1\langle 110\rangle} = \upsilon_{t\langle 100\rangle}$.

Table 1. Abrupt changes of sound velocities and their relations at valence transition in the $Sm_{0.85}Y_{0.15}S$ (%) alloy

Direction in the monocrystal	$\Delta\upsilon_L/\upsilon_L$	$\Delta\upsilon_\ell/\upsilon_\ell$	$\Delta\upsilon_t/\upsilon_t$	$\frac{\Delta(\upsilon_L/\upsilon_t)}{(\upsilon_L/\upsilon_t)}$	$\frac{\Delta(\upsilon_\ell/\upsilon_t)}{(\upsilon_\ell/\upsilon_t)}$	$\frac{\Delta(\upsilon_L/\upsilon_\ell)}{(\upsilon_L/\upsilon_\ell)}$
polycrystal	-22.5	-45.2	+6.7	-29.0	-50.0	+26.5
<100>	-12.8	-57.4	+8.3	-4.6	-53.6	+42.9
<110>	-25.0	-45.2	+11.6**	-13.8*	-45.5*	+23.9
				-35.4**	-31.8**	
<111>	-32.0	-42.9	+9.8	-40.0	-47.4	+14.3

Note: * $\upsilon_t = \upsilon_{t_1}$, ** $\upsilon_t = \upsilon_{t_2}$, signs "+","–" see explanations in the text

Relations of sound velocities υ_L/υ_t, υ_ℓ/υ_t and υ_L/υ_ℓ for specific directions in the monocrystal and for the polycrystal depending upon the composition of the mixed system are presented in Figure 2 (a, b, c). Concentration dependences of these parameters are different from functions υ (x) in Figure 1 and can be reduced to the following: in the semiconductor phase of the $Sm_{1-x}Y_xS$ alloy ($x < 0{,}15$) with the growth of yttrium concentration all relations of sound velocities decrease linearly; in the metallic phase these relations are non-linear with the change of x, and functions υ_L/υ_ℓ (x) have minimums near $x \approx 0.4$ for three directions in the monocrystal and for the $Sm_{1-x}Y_xS$ polycrystal; values of sound velocities relations in the polycrystal take the intermediate position between the values of corresponding relations in the monocrystal; during the transition from the semiconductor into metallic

phase ($x = x_c$) υ_L/υ_t and υ_ℓ/υ_t decrease abruptly and υ_L/υ_ℓ increases. The values of changes of these relations are shown in Table 1 and approximately amount to 0.5% - 50%; the important condition for the acoustic problem of auxetics: relations $\left(\upsilon_L/\upsilon_{t_2}\right)_{\langle 110\rangle}, \left(\upsilon_L/\upsilon_t\right)_{\langle 111\rangle}$ in the interval of concentration values $0.15 < x < 0.40$ become less than one; $\left(\upsilon_\ell/\upsilon_{t_2}\right)_{\langle 110\rangle} < 1$ in the whole metallic phase of the alloy and in the pure yttrium sulfide (YS); the curve $\left(\upsilon_\ell/\upsilon_t\right)_{\langle 111\rangle}(x)$ almost repeats the curve $\left(\upsilon_\ell/\upsilon_{t_2}\right)_{\langle 110\rangle}(x)$ for $x > x_c$ and only slightly exceeds the one in the interval $0.42 < x < 0.80$; near the valence transition from the metallic phase and other sound velocities relations (υ_ℓ/υ_t) decrease to values lower than one.

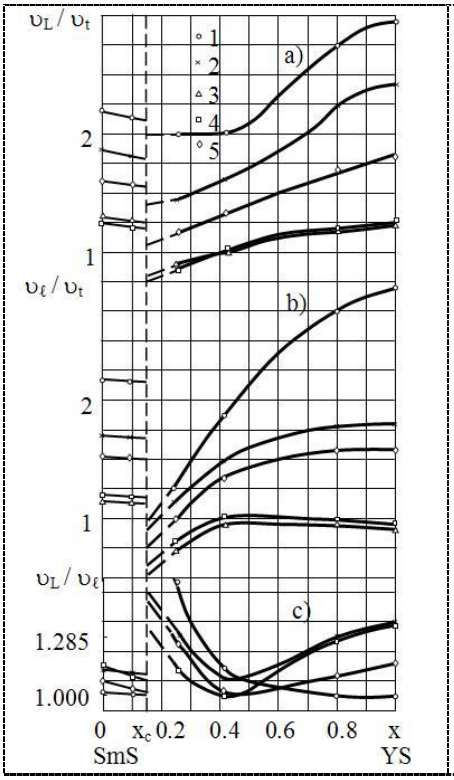

Figure 2. Relations of propagation velocities of longitudinal and traverse elastic waves depending upon the $Sm_{1-x}Y_xS$ alloy composition. 1, 2, 3, 4 – monocrystal, 5 – polycrystal. Directions in the monocrystal: 1 - <100>, 2 – <110.001>, 3 – $<110.1\bar{1}0>$, 4 – <111>

In Table 2 we present anisotropic Young's moduli, shear moduli, Poisson's ratios of $Sm_{1-x}Y_xS$ alloy monocrystals and also jumps of the mentioned elastic parameters at the valence transition from the semiconductor into the metallic phase ($x = x_c$). Anisotropy of modules $E_{\langle 100\rangle} > E_{\langle 110\rangle} > E_{\langle 111\rangle}$, $G_{\langle 100\rangle} < G_{\langle 110\rangle} < G_{\langle 111\rangle}$ is retained for all compositions of the studied alloy monocrystals including the pure primary components. The established inequalities between the elastic moduli are characteristic of cubic ion monocrystals with lattices of the NaCl type. In a number of cases anisotropy of elastic properties is characterized by relation of Young's moduli $E_{\langle 100\rangle}/E_{\langle 110\rangle}$ for two crystallographic directions. If we analyze results of Table 2 from this point of view the relation of the given moduli will make: SmS ($E_{<100>}/E_{<110>} = 1.62$), $Sm_{0.91}Y_{0.09}$ ($E_{<100>}/E_{<110>} = 1.62$), $Sm_{0.75}Y_{0.25}$ ($E_{<100>}/E_{<110>} = 1.29$), $Sm_{0.58}Y_{0.42}S$ ($E_{<100>}/E_{<110>} = 1.54$), $Sm_{0.80}Y_{0.20}S$ ($E_{<100>}/E_{<110>} = 2.36$), YS ($E_{<100>}/E_{<110>} = 2.63$). This way, we can state that compositions of $Sm_{0.75}Y_{0.25}S$ and $Sm_{0.58}Y_{0.42}S$ alloys with negative Poisson's ratios have decreased anisotropy of elastic properties.

Anisotropic Poisson's ratios of $Sm_{1-x}Y_xS$ monocrystals (Table 2) fulfil inequality characteristic for cubic monocrystals (except for $Sm_{0.75}Y_{0.25}S$ and $Sm_{0.58}Y_{0.42}S$): $\sigma_{\langle 110.001\rangle} < \sigma_{\langle 100\rangle} < \sigma_{\langle 111\rangle} < \sigma_{\langle 110.1\bar{1}0\rangle}$. Alloy compositions with yttrium concentration of $0.15 \le x \le 0.29$ have negative Poisson's ratios in all three specific crystallographic directions. When extrapolating the results for the metallic phase, minimum values of Poisson's ratios are observed at critical yttrium concentration ($x = x_c$) and Poisson's ratio equals $\sigma_{\langle 100\rangle}(x_c) = -0.98.$ for direction <100>.

Table 2. Anisotropic Young's, shear (GPa) moduli, Poisson's ratios and their relative jumps (%) at the valence transition in the monocrystal of the $Sm_{1-x}Y_xS$ alloy

	$E_{<100>}$	$E_{<110>}$	$E_{<111>}$	$G_{<100>}$	$G_{<110>}$	$G_{<111>}$	$\sigma_{<100>}$	$\sigma_{<110.001>}$	$\sigma_{\langle 110.1\bar{1}0\rangle}$	$\sigma_{<111>}$
YS	240.62	91.54	75.87	27.70	44.32	55.41	0.086	0,033	0.652	0.457
SmS	124.92	77.22	68.50	26.90	38.61	41.69	0.086	0,053	0.435	0.273
$Sm_{0.91}Y_{0.09}S$	126.61	78.57	69.74	28.00	38.38	43.80	0.038	0,024	0.403	0.245
$Sm_{0.75}Y_{0.25}S$	58.55	45.28	42.10	32.00	47.07	55.84	-0.671	-0,519	-0.293	-0.342
$Sm_{0.58}Y_{0.42}S$	123.23	80.15	71.79	34.70	49.76	58.18	-0.299	-0,195	0.154	0.034
$Sm_{0.20}Y_{0.80}S$	218.15	92.48	77.59	29.00	45.40	55.95	0.044	0,019	0.595	0.338
$Sm_{0.85}Y_{0.15}S$		ΔE/E			ΔG/G				Δσ/σ	
	-82.4	-78.1	-83.3	-7.0	+14.5	+16.7	-19800	-3750	-247.5	-385.7

Table 3 presents density (ρ), elastic (B, G, E, σ) properties, acoustic $(\upsilon_L, \upsilon_\ell, \upsilon_t, \bar{\upsilon}_{sq}, \bar{\upsilon})$ properties, plasticity-fragility criterion (B/G) and Grüneisen parameter (γ) of $Sm_{1-x}Y_xS$ alloy polycrystals. Here we provide values and signs of relative jumps of all Table 3 parameters at the critical concentration of alloy components ($Sm_{0.85}Y_{0.15}S$). All alloy compositions are characterized by greater resistance to unilateral pressure deformation in comparison to uniform compression (E > B), and sound velocities make "regular" string $\upsilon_L > \upsilon_\ell > \upsilon_t$ and $\bar{\upsilon}_{sq} > \bar{\upsilon}$. SmS is more fragile than YS but at the same time it can be easily turned into an "absolutely fragile" alloy ($B/G \to 0$) with a comparatively small addition of the second component (x = 0.15). This condition is likely to prevent us from studying the mechanical properties of the $Sm_{0.85}Y_{0.15}S$ alloy close to the critical point. Grüneisen parameter depending upon the alloy composition demonstrates behavior similar to function B/G (x) and at critical concentration equals $\gamma\ (0.15) \approx 0$. If we take into consideration the fact that at the electronic phase transition Poisson's ratio is close to the limit value σ = -0.82, we observe a demonstration of three important factors: one of the lowest known Poisson's ratio values, record of absolute fragility and the almost complete harmonization of the interatomic oscillations. The given combination requires further understanding. Abrupt changes of the elastic and acoustic parameters of the $Sm_{0.85}Y_{0.15}S$ alloy polycrystal presented in Table 3 are quite large and can be related to similar changes for the monocrystal of the same alloy composition.

Values of sound velocities and Poisson's ratios relations obtained by formulas (1) – (4) for elastically isotropic polycrystals $Sm_{1-x}Y_xS$ are given in Table 4. From this table we can clearly see that for positive σ_x, σ_y or σ_{xy} a positive value of the σ_{z_1} root is obtained and, vice versa, when σ_x, σ_y and σ_{xy} are negative a negative value of σ_{z_2} is obtained.

Table 3. Density, elastic moduli and their relation, Poisson's ratio, sound velocities, Grüneisen parameter of the $Sm_{1-x}Y_xS$ polycrystal and changes of the given characteristics at the critical concentration of components (%)

	ρ, 10^3	B	G	E	σ	υ_L	υ_ℓ	υ_t	$\bar{\upsilon}_{sq}$	$\bar{\upsilon}$	B/G	γ
	$kg \cdot m^{-3}$	GPa				$m \cdot s^{-1}$						
YS	4.830	96.95	48.88	125.54	0.284	5794	5098	3181	4235	3546	1.983	1.679
SmS	5.690	50.33	36.50	88.18	0.208	4171	3937	2533	3174	2800	1.379	1.316
$Sm_{0.91}Y_{0.09}S$	5.780	45.67	38.28	89.76	0.172	4090	3941	2573	3161	2832	1.193	1.186
$Sm_{0.75}Y_{0.25}S$	6.090	8.33	48.05	49.32	-0.487	3448	2846	2809	3037	2969	0.173	0.222
$Sm_{0.58}Y_{0.42}S$	5.820	25.68	50.36	91.36	-0.093	3994	3962	2942	3330	3169	0.510	0.597
$Sm_{0.20}Y_{0.80}S$	5.183	79.67	48.88	121.74	0.245	5286	4846	3071	3950	3407	1.630	1.477
$Sm_{0.85}Y_{0.15}S$	+8.2	-100.0	+13.8	-92.2	-647.6	-21.9	-43.8	+6.7	-7.3	+2.6	-100.0	-78.2

Table 4. Relations of sound velocities and calculated relations of Poisson's ratios with their application by formulas (1) – (4) for the polycrystals of the $Sm_{1-x}Y_xS$ system

	x*	y	z	σ_x	σ_y	σ_{xy}	σ_{z_1}	σ_{z_2}
YS	1.8214	1.6026	1.1365	0.284	0.284	0.284	0.284	-0.397
SmS	1.6467	1.5543	1.0594	0.208	0.208	0.208	0.208	-0.262
$Sm_{0.91}Y_{0.09}S$	1.5896	1.5317	1.0378	0.173	0.173	0.173	0.172	-0.208
$Sm_{0.75}Y_{0.25}S$	1.2275	1.0132	1.2115	-0.487	-0.487	-0.487	0.327	-0.487
$Sm_{0.58}Y_{0.42}S$	1.3576	1.3467	1.0081	-0.093	-0.093	-0.093	0.085	-0.093
$Sm_{0.20}Y_{0.80}S$	1.7213	1.5780	1.0908	0.245	0.245	0.245	0.245	-0.325

Note: * sign $x = \upsilon_L/\upsilon_t$

4. Conclusions

1. Anisotropy of sound velocities has been determined for pure components and various compositions of alloy $Sm_{1-x}Y_xS$ monocrystals: $\upsilon_{L\langle 100\rangle} > \upsilon_{L\langle 110\rangle} > \upsilon_{L\langle 111\rangle}$, $\upsilon_{\ell\langle 100\rangle} > \upsilon_{\ell\langle 110\rangle} > \upsilon_{\ell\langle 111\rangle}$, $\upsilon_{t\langle 100\rangle} < \upsilon_{t\langle 111\rangle} < \upsilon_{t\langle 110\rangle}$. Anisotropy of longitudinal wave propagation velocities is reflected in the anisotropy of Young's modulus and that of traverse waves – in the shear modulus anisotropy.
2. The concentration dependences of sound velocities, their ratios, elastic moduli and Poisson's ratios for mono- and polycrystals of the $Sm_{1-x}Y_xS$ alloy were studied. All these characteristics change their values abruptly (in a discontinuous way) at the critical concentration of yttrium sulfide in samarium sulfide $x_c = 0.15$ (transition from the semiconductor phase of the alloy into the metallic one). Significant changes are demonstrated by Poisson's ratios (for example, $\Delta\sigma/\sigma_{<100>} \approx 2\cdot10^4$ %).
3. It has been confirmed that the $Sm_{1-x}Y_xS$ alloys with concentration of components $0.15 < x < 0.75$ are partial auxetics ($\sigma_{<100>}$ of the monocrystal < 0), and in the narrower interval of concentrations ($0.15 < x < 0.50$) are (complete) auxetics (σ of the polycrystal < 0).

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