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Elastic properties of solid solutions with intermediate valence $Sm_{1-x}Y_xS$

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Abstract. The given article considers acoustic analogues of elasticity theory ratios determining Poisson's ratios of $Sm_{1-x}Y_xS$ alloy by their elastic parameters. The article discusses behavior of sound velocities, elastic moduli, Poisson's ratios, Grüneisen parameter and brittleness-plasticity criterion ratios depending on the concentration of alloy components including valence transition from semiconductors into the metal phase.

Introduction

Over recent years there is increased interest to the studies of materials with negative Poisson's ratio ($\sigma < 0$) which are called "auxetics" [1]. The scientists study the mechanisms and establish the criteria of negative Poisson's ratios appearance in isotropic and anisotropic solids [2]. The limit values $\sigma = 0.5$ and $\sigma = -1$ in ideal elastic continuous media are analyzed from the point of view of physical acoustics as its methods are widely used in experimental studies of elastic properties of various materials [3]. Previously we completed 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 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 are equivalent. We used the data on elastic parameters of polycrystals obtained from rigidity constants compliance constants of monocrystals in Voigt-Royce-Hill approximation [5].

In the given work we study the interrelation of sound velocities and Poisson's ratios relations on 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 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 the valence transition $Sm^{2+} \rightarrow Sm^{3+}$ [7] and study of materials with intermediate valence in relation to their simultaneous demonstration of anomalous properties is of special interest.

Calculation ratios

The most frequent calculation ratios for the Poisson's ratios of isotropic bodies are the following interrelations [1, 8]:

$$\sigma = \frac{3B - 2G}{6B + 2G} \quad (1)$$

$$\sigma = \frac{E}{2G} - 1 \tag{2}$$

$$\sigma = 0.5 - \frac{E}{6B} \tag{3}$$

$$\upsilon_L = \left[\frac{E(1-\sigma)}{\rho(1+\sigma)(1-2\sigma)} \right]^{1/2}. \tag{4}$$

Here B – bulk modulus, G – shear modulus, υ_L –velocity of propagation longitudinal elastic waves, E – Young modulus, and ρ – density of material.
The provided expressions (1) – (4) can be transformed to the formulas for σ only through the relations of sound velocities:

$$\sigma_x = \frac{x^2-2}{2x^2-2}, \quad x = \frac{\upsilon_L}{\upsilon_t} \tag{5}$$

$$\sigma_y = 0.5y^2 - 1, \quad y = \frac{\upsilon_\ell}{\upsilon_t} \tag{6}$$

$$\sigma_{xy} = 0.5 - \frac{y^2}{6x^2-8} \tag{7}$$

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

where υ_t – velocity of propagation traverse elastic waves, υ_ℓ – velocity of longitudinal waves propagation in the core.
There are no experimental values of elastic moduli of $Sm_{1-x}Y_xS$ polycrystals and sound velocities in them. That's why in the given 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 works [2, 6].
Velocities of purely longitudinal and traverse waves propagation for isotropic elastic bodies and in three specific directions of cubic monocrystals of the hybrid system $Sm_{1-x}Y_xS$ was found through the known relations of elasticity theory and physical acoustics [5, 8, 11, 12].
Grüneisen parameter γ, anharmonicity measure of interatomic oscillations and non-linearity of interatomic interrelation forces were calculated according to the previously established formula [12]:

$$\gamma = \frac{3}{2}\left(\frac{3\upsilon_L^2 - 4\upsilon_t^2}{\upsilon_L^2 + 2\upsilon_t^2} \right). \tag{9}$$

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 provided data bring us to a number of basic conclusions: functions υ_L (x), υ_t (x) are linear in both phases of the studied system; dependence υ_ℓ (x) is linear only in the 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 ($\upsilon_{L\langle100\rangle} > \upsilon_{L\langle110\rangle} > \upsilon_{L\langle111\rangle}$, $\upsilon_{\ell\langle100\rangle} > \upsilon_{\ell\langle110\rangle} > \upsilon_{\ell\langle111\rangle}$) and is different for the traverse waves ($\upsilon_{t_2\langle110\rangle} > \upsilon_{t\langle111\rangle} > \upsilon_{t\langle100\rangle} = \upsilon_{t_1\langle110\rangle}$); under the isostructural transition all sound velocities change abruptly but differently in terms of quality and quantity: velocities of longitudinal waves decrease, velocities of traverse waves increase. The data on the given fact are given in Table 1 ("+" here corresponds to the intermittent growth of sound velocity under the alloy transition from the semiconductor phase into the metallic and "–" corresponds to the intermittent decrease).

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 Fig. 2 (a, b, c). Concentration dependences of these parameters are different from functions υ (x) in Fig. 1 and can be reduced to the following: in the semiconductor phase of $Sm_{1-x}Y_xS$ 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 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 $Sm_{1-x}Y_xS$ 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 the metallic phase ($x = x_c$) υ_L/υ_t and υ_ℓ/υ_t decrease intermittently and υ_L/υ_ℓ increase. The values of changes of these relations are shown in Table 1 and make and make approximately from 0.5% to 50%; the important for the acoustic problem of auxetics condition: relations $(\upsilon_L/\upsilon_{t_2})_{\langle110\rangle}$, $(\upsilon_L/\upsilon_t)_{\langle111\rangle}$ in the interval of concentration values 0.15 < x < 0.40 become less than one; $(\upsilon_\ell/\upsilon_{t_2})_{\langle110\rangle} < 1$ in the whole metallic phase of the alloy and in the pure yttrium sulfide (YS); curve $(\upsilon_\ell/\upsilon_t)_{\langle111\rangle}(x)$ almost repeats curve $(\upsilon_\ell/\upsilon_{t_2})_{\langle110\rangle}(x)$ under $x > x_c$ and only slightly exceeds 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.

In Table 2 we present anisotropic Young moduli, shear moduli, Poisson's ratios of $Sm_{1-x}Y_xS$ alloy monocrystals and also jumps of the mentioned elastic parameters under valence transition from the semiconductor into the metallic phase ($x = x_c$). Anisotropy of modules $E_{\langle100\rangle} > E_{\langle110\rangle} > E_{\langle111\rangle}$, $G_{\langle100\rangle} < G_{\langle110\rangle} < G_{\langle111\rangle}$ is retained for all compositions of the studied alloy monocrystals including the pure primary components. The established inequities between the elastic moduli are characteristic of cubic ion monocrystals with lattices of NaCl type. In a number of cases anisotropy of elastic properties is characterized by relation of Young moduli $E_{\langle100\rangle}/E_{\langle110\rangle}$ for two crystallographic directions. If we analyze results of Table 2 from this point of view 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 $Sm_{0.58}Y_{0.42}S$ alloy with negative Poisson's ratios have decreased anisotropy of elastic properties.

Anisotropic Poisson's ratios of $Sm_{1-x}Y_xS$ monocrystals (Table 2) make inequity characteristic for cubic monocrystals (for the exception of $Sm_{0.75}Y_{0.25}S$ and $Sm_{0.58}Y_{0.42}S$): $\sigma_{\langle110.001\rangle} < \sigma_{\langle100\rangle} < \sigma_{\langle111\rangle} < \sigma_{\langle110.1\bar{1}0\rangle}$. 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 from the results for the metallic phase minimum values of Poisson's ratios are observed under critical yttrium concentration ($x = x_c$) and Poisson's ratio equals $\sigma_{\langle100\rangle}(x_c) = -0.98$. for direction <100>.

Table 3 presents density (ρ), elastic (B, G, E, σ), 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 under 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 the "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 "absolutely fragile" alloy (B/G → 0) with addition of comparatively small addition of second component (x = 0.15). This condition is likely to prevent us from studying the mechanical properties of $Sm_{0.85}Y_{0.15}S$ alloy closely to the critical point. Grüneisen parameter depending upon alloy composition demonstrates behavior similar to function B/G (x) and under critical concentration equals γ (0.15) ≈ 0. If we take into consideration the fact that under electronic phase transition Poisson's ratio reaches its close to limit value σ = -0.82, we observe demonstration of three "mighty" factors: one of the lowest known Poisson'a ratio values, record absolute fragility and almost complete harmonization of interatomic oscillations. The given combination requires further understanding. Abrupt changes of elastic and acoustic parameters of $Sm_{0.85}Y_{0.15}S$ 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 (5) – (8) for elastically isotropic alloys polycrystals $Sm_{1-x}Y_xS$ are given in Table 4. From this table we can clearly see that that under positive σ_x, σ_y or σ_{xy} positive value of σ_{z_1} root is actual and, vice versa, when σ_x, σ_y and σ_{xy} are negative the negative value of σ_{z_2} is actual.

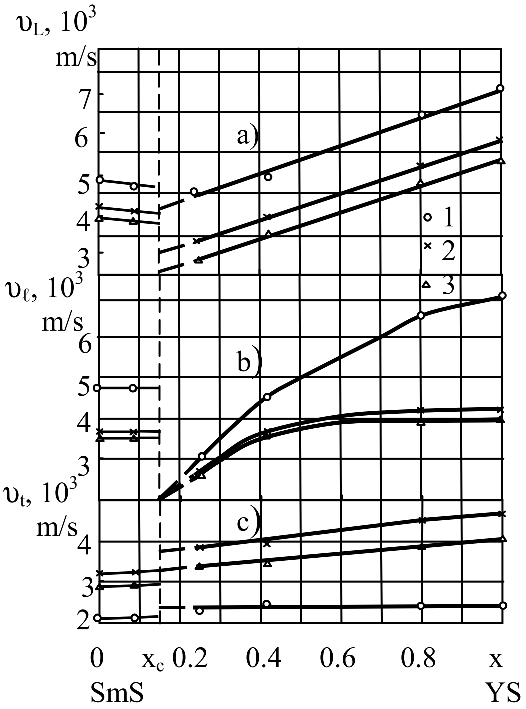

Fig. 1. Changing of propagation velocities of longitudinal (υ_L, υ_ℓ) and traverse (υ_t) elastic waves in specific directions of $Sm_{1-x}Y_xS$ monocrystal under valence transition.
1 – <100>, 2 – <110>, 3 – <111>
x_c – critical concentration, $\upsilon_{t_1\langle 110\rangle} = \upsilon_{t\langle 100\rangle}$.

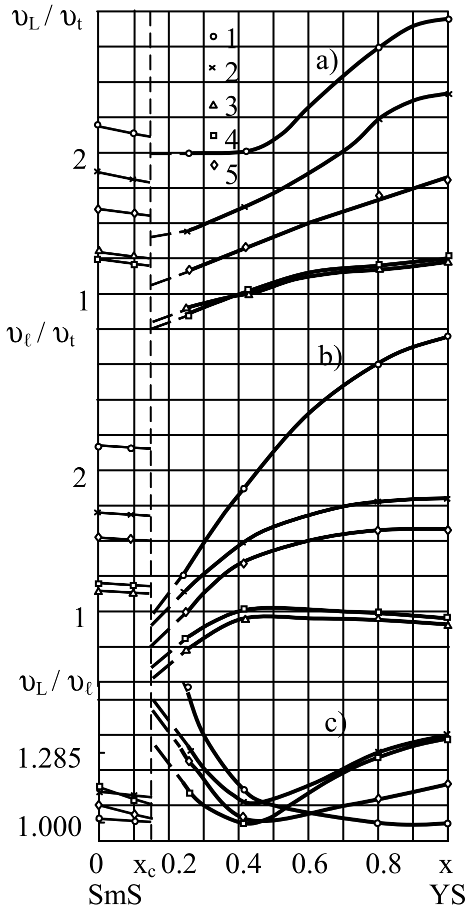

Fig. 2. Relations of propagation velocities of longitudinal and traverse elastic waves depending upon $Sm_{1-x}Y_xS$ alloy composition. 1, 2, 3, 4 – monocrystal, 5 – polycrystal. Directions in the monocrystal:
1 - <100>, 2 – <110.001>, 3 – $<110.1\bar{1}0>$,
4 – <111>

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

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

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

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

	$E_{<100>}$	$E_{<110>}$	$E_{<111>}$	$G_{<100>}$	$G_{<110>}$	$G_{<111>}$	$\sigma_{<100>}$	$\sigma_{<110.001>}$	$\sigma_{\langle 110.1\bar{1}0\rangle}$	$\sigma_{<111>}$
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

	$E_{<100>}$	$E_{<110>}$	$E_{<111>}$	$G_{<100>}$	$G_{<110>}$	$G_{<111>}$	$\sigma_{<100>}$	$\sigma_{<110.001>}$	$\sigma_{\langle 110.1\bar{1}0\rangle}$	$\sigma_{<111>}$
$Sm_{0.75}Y_{0.25}S$	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
YS	240.62	91.54	75.87	27.70	44.32	55.41	0.086	0,033	0.652	0.457
$Sm_{0.85}Y_{0.15}S$	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. Density, elastic moduli and their relation, Poisson's ratio, sound velocities, Grüneisen parameter of $Sm_{1-x}Y_xS$ polycrystal and changes of the given characteristics under 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·m^{-3}	GPa				m·s^{-1}						
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
YS	4.830	96.95	48.88	125.54	0.284	5794	5098	3181	4235	3546	1.983	1.679
$Sm_{0.85}Y_{0.15}S$	+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 (5) – (8) for the polycrystals of $Sm_{1-x}Y_xS$ system

	x*	y	z	σ_x	σ_y	σ_{xy}	σ_{z_1}	σ_{z_2}
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
YS	1.8214	1.6026	1.1365	0.284	0.284	0.284	0.284	-0.397

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

Conclusion

1. We determined anisotropy of sound velocities for pure components and all 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 waves propagation velocities is repeated in anisotropy of Young modulus and that of traverse waves – to shear modulus anisotropy.
2. We determined concentration dependences of sound velocities, their relations, elastic moduli and Poisson's ratios of mono- and polycrystals of $Sm_{1-x}Y_xS$ alloy. All enumerated characteristics change their value abruptly (intermittently) under critical concentration of yttrium sulfide in samarium sulfide $x_c = 0.15$ (transition from the semiconductor phase of the alloy into the metallic one). The most significant changes are demonstrated by Poisson's ratios (for example, $\Delta\sigma/\sigma_{<100>} \approx 2\cdot 10^4$ %).
3. Compositions of $Sm_{1-x}Y_xS$ alloy with concentration of components $0.15 < x < 0.75$ are axial auxetics ($\sigma_{<100>}$ of the monocrystal < 0), and in the narrower interval of concentrations ($0.15 < x < 0.50$) proper (full) auxetics (σ of the polycrystal < 0).

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