Elasticity of the Sm$_{1-x}$Y$_x$S 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$_x$S 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 $\sigma$ 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$_x$S 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$_x$S 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 $\sigma$ expressed through the sound velocities:

$$
\sigma_x = \frac{x^2 - 2}{2x^2 - 2}, \quad x = \frac{v_t}{v_l} \tag{1}
$$

$$
\sigma_y = 0.5y^2 - 1, \quad y = \frac{v_t}{v_l} \tag{2}
$$

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

$$
\sigma_{x_{12}} = \frac{-(z^2 - 1) \pm \sqrt{\left(z^2 - 1\right)^2 + 8z^2(z^2 - 1)}}{4z^2}, \quad z = \frac{v_t}{v_l} \tag{4}
$$

where $v_t$ – velocity of propagation for transverse elastic waves, $v_l$ – velocity of longitudinal waves propagation in the plug, $v_{l1}$ – velocity of propagation longitudinal elastic waves.

However, no experimental values are known for elastic moduli of Sm1-xYxS 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 (ВV, GV), Royce (ВR, GR), Voigt-Royce-Hill (ВVRH, GVRH) [5], G. Peresada (GPer) [9], K.S. Alexandrov (GAл) [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 Sm1-xYxS were found through the known relations of elasticity theory and physical acoustics [5, 8, 11, 12].

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

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

3. Results and their discussion

Changes of velocities of elastic waves propagation in crystallographic directions <100>, <110> and <111> of cubic monocrystals Sm1-xYxS depending on their composition are presented in Figure 1 (a, b, c). The obtained data provide us with a number of basic conclusions: functions $v_{l1}(x)$, $v_{t1}(x)$ are linear in both phases of the studied system; dependence $v_{t2}(x)$ is linear only in semiconductor phase Sm1-xYxS; with the growth of yttrium concentration at the initial stage ($0 < x \leq x_c$, 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 ($v_{l_{100}} > v_{l_{110}} > v_{l_{111}} > v_{l_{101}} > v_{l_{110}}$) and is different for traverse waves ($v_{t_{100}} > v_{t_{110}} > v_{t_{111}} = v_{t_{110}}$); 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 discontinuous growth of sound velocity at the alloy transition from the semiconductor phase into the metallic one and “–”corresponds to the discontinuous decrease).
Concentration dependence of propagation velocities for longitudinal ($v_L$, $v_\ell$) and traverse ($v_t$) elastic waves in specific directions of Sm$_{1-x}$Y$_x$S monocrystals. 

1 – <100>, 2 – <110>, 3 – <111>, $x_c$ – critical concentration, $v_{t(110)} = v_{t(001)}$.

### 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 | $\Delta v_L / v_L$ | $\Delta v_\ell / v_\ell$ | $\Delta v_t / v_t$ | $\Delta (v_L/v_\ell)$ | $\Delta (v_L/v_t)$ | $\Delta (v_\ell/v_t)$ |
|------------------------------|-------------------|-----------------|-----------------|-------------------|-------------------|-------------------|
| 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: $^* v_t = v_\ell$, $^\ast v_t = v_\ell$, signs "+", "−" see explanations in the text.

Relations of sound velocities $v_L/v_\ell$, $v_\ell/v_t$, and $v_L/v_t$ 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 $v(x)$ in Figure 1 and can be reduced to the following: in the semiconductor phase of the Sm$_{1-x}$Y$_x$S 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 $v_L/v_\ell (x)$ have minimums near $x \approx 0.4$ for three directions in the monocrystal and for the Sm$_{1-x}$Y$_x$S 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 \((x = x_c)\) \(v_L/v_t\) and \(v_t/v_L\) decrease abruptly and \(v_L/v_t\) 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 \((v_L/v_t)_{<100}\), \((v_t/v_L)_{<110}\) in the interval of concentration values \(0.15 < x < 0.40\) become less than one; \((v_L/v_t)_{<110}\) <1 in the whole metallic phase of the alloy and in the pure yttrium sulfide (YS); the curve \((v_t/v_L)_{<110}(x)\) almost repeats the curve \((v_t/v_L)_{<110}(x)\) 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 \((v_t/v_L)\) 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\(_x\)S alloy composition. 1, 2, 3, 4 – monocrystal, 5 – polycrystal. Directions in the monocrystal: 1 - <100>, 2 – <110>, 3 – <110>110, 4 – <111>](image)

In Table 2 we present anisotropic Young’s moduli, shear moduli, Poisson’s ratios of Sm\(_{1-x}\)Y\(_x\)S 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 \(E_{<100>} > E_{<110>} > E_{<111>}\), \(G_{<100>} < G_{<110>} < G_{<111>}\) 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 \(E_{<100>} / E_{<110>}\) 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 \((E_{<1100>} / E_{<1110>} = 1.62)\), Sm\(_{0.91}\)Y\(_{0.09}\) \((E_{<1100>} / E_{<1110>} = 1.62)\), Sm\(_{0.72}\)Y\(_{0.28}\) \((E_{<1100>} / E_{<1110>} = 1.29)\), Sm\(_{0.58}\)Y\(_{0.42}\) \((E_{<1100>} / E_{<1110>} = 1.54)\), Sm\(_{0.80}\)Y\(_{0.20}\) \((E_{<1100>} / E_{<1110>} = 2.36)\), YS \((E_{<1100>} / E_{<1110>} = 2.63)\). 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$_x$S monocrystals (Table 2) fulfill inequality characteristic for cubic monocrystals (except for Sm$_{0.75}$Y$_{0.25}$S and Sm$_{0.58}$Y$_{0.42}$S): $\sigma_{\langle 100 \rangle} < \sigma_{\langle 100 \rangle} < \sigma_{\langle 111 \rangle}$. Alloy compositions with yttrium concentration of $0.15 \leq x \leq 0.29$ 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$_x$S alloy

|          | $E_{\langle 100 \rangle}$ | $E_{\langle 110 \rangle}$ | $E_{\langle 111 \rangle}$ | $G_{\langle 100 \rangle}$ | $G_{\langle 110 \rangle}$ | $G_{\langle 111 \rangle}$ | $\sigma_{\langle 100 \rangle}$ | $\sigma_{\langle 100.001 \rangle}$ | $\sigma_{\langle 10.1 \rangle}$ | $\sigma_{\langle 111 \rangle}$ |
|----------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|-------------------------------|---------------------------------|--------------------------------|-------------------------------|
| 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 | $\Delta E/E$              | $\Delta G/G$              | $\Delta \sigma/\sigma$   |                           |                           |                           |                               |                                 |                                 |                                |
|          | -82.4                     | -78.1                     | -83.3                     | -7.0                      | +14.5                     | +16.7                     | +19800                        | -3750                           | -247.5                          | -385.7                         |

Table 3 presents density ($\rho$), elastic (B, G, E, $\sigma$) properties, acoustic ($\nu_L$, $\nu_T$, $\nu_{\text{sq}}$, $\nu_{\text{l}}$) properties, plasticity-fragility criterion (B/G) and Grüneisen parameter ($\gamma$) of Sm$_{1-x}$Y$_x$S 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 $\nu_L > \nu_T > \nu_{\text{sq}} > \nu_{\text{l}}$. 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 $\gamma (0.15) = 0$. If we take into consideration the fact that at the electronic phase transition Poisson’s ratio is close to the limit value $\sigma = -0.82$, 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$_x$S are given in Table 4. From this table we can clearly see that for positive $\sigma_x$, $\sigma_y$ or $\sigma_{xy}$ a positive value of the $\sigma_{z}$ root is obtained and, vice versa, when $\sigma_x$, $\sigma_y$ and $\sigma_{xy}$ are negative a negative value of $\sigma_{z}$ is obtained.

Table 3. Density, elastic moduli and their relation, Poisson’s ratio, sound velocities, Grüneisen parameter of the Sm$_{1-x}$Y$_x$S poly-
crystal and changes of the given characteristics at the critical
concentration of components (%)

| Component | $\rho$, $10^3$ kg m$^{-3}$ | B | G | E | $\sigma$ | $v_L$ | $v_t$ | $v_{st}$ | $v$ | B/G | $\gamma$ |
|-----------|------------------|---|---|---|---|---|---|---|---|---|---|
| YS        | 5.690            | 45.67 | 38.28 | 89.76 | 0.208 | 3941 | 2573 | 3161 | 2832 | 1.193 | 1.186 |
| SmS       | 5.820            | 25.68 | 50.36 | 91.36 | -0.093 | 3962 | 2942 | 3330 | 3169 | 0.173 | 0.222 |
| Sm$_{0.91}$Y$_{0.09}$S | 5.780 | 4.850 | 49.32 | -0.487 | 3448 | 2846 | 2809 | 3037 | 2969 | 0.173 | 0.222 |
| Sm$_{0.75}$Y$_{0.25}$S | 6.090 | 8.33 | 48.05 | 49.32 | -0.093 | 3994 | 2942 | 3330 | 3169 | 0.510 | 0.597 |
| Sm$_{0.58}$Y$_{0.42}$S | 5.820 | 25.68 | 50.36 | 91.36 | -0.093 | 3994 | 2942 | 3330 | 3169 | 0.510 | 0.597 |
| Sm$_{0.20}$Y$_{0.80}$S | 5.183 | 79.67 | 48.88 | 121.74 | 0.245 | 3994 | 2942 | 3330 | 3169 | 0.510 | 0.597 |
| Sm$_{0.85}$Y$_{0.15}$S | +8.2 | -100.0 | +13.8 | -92.2 | -647.6 | 121.74 | 0.245 | 3994 | 2942 | 3330 | 3169 | 0.510 | 0.597 |

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$_x$S system

| Component | $x^*$ | $y$ | $z$ | $\sigma_x$ | $\sigma_y$ | $\sigma_{xy}$ | $\sigma_z$ |
|-----------|-------|---|---|---|---|---|---|
| YS        | 1.8214 | 1.6026 | 1.1365 | 0.284 | 0.284 | 0.284 | -0.397 |
| SmS       | 1.6467 | 1.5543 | 1.0594 | 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 | -0.208 |
| 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 | -0.325 |

Note: $^*$ sign $x$ = $v_L$/$v_t$
4. Conclusions
1. Anisotropy of sound velocities has been determined for pure components and various compositions of alloy Sm$_{1-x}$Y$_x$S monocrystals: $v_{L(100)} > v_{L(110)} > v_{L(111)}$, $v_{L(100)} > v_{L(110)} > v_{L(111)}$, $v_{L(100)} < v_{L(110)} < v_{L(111)}$. 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$_x$S 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$_x$S 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 ($\sigma$ of the polycrystal < 0).

References
[1] Alderson KL, Alderson A, Grima JN, Wojciechowski KW 2014 Phys. Status Solidi (b) 250 263.
[2] Goldstein RV, Gorodtsov VA, Lisovenko DS 2013 Phys. Status Solidi (b) 250 2038.
[3] Lipsett AW, Beltzer AI 1988 J. Acoust. Soc. Am. 84 2179.
[4] Belomestnykh VN, Soboleva EG 2012 7th International Forum on Strategic Technology (IFOST - 2012) 1 499.
[5] Tesleva E, Belkova T 2014 Applied Mechanics and Materials 682 519.
[6] Hailing Tu, Saunders GA and other 1984 J. Phys. C: Solid State Phys. 17 4559.
[7] Belomestnykh VN, Tesleva EP 2012 7th International Forum on Strategic Technology (IFOST - 2012) 2 381.
[8] Frantsevich IN, Voronov FF and Bakuta SA 1982 Elastic constants and elastic moduli of metals and non-metals Kiev 286.
[9] Peresada GL 1971 Phys. Status Solidi A4 K 23.
[10] Alexandrov KS 1967 Reports of Academy of Sciences USSR 176 295.
[11] Soboleva EG, Igisheva AL and Krit TB 2015 IOP Conf. Series: Materials Science and Engineering 91 1-7
[12] Belomestnykh VN Tesleva EP and Soboleva EG 2008 Technical Physics Letters 34 867.