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FURTHER INVESTIGATIONS ON THE TEMPERATURE-DEPENDENCE OF MAGNETIC SUSCEPTIBILITY AND THERMOGRAVIMETRY OF STOICHIOMETRIC ANTIMONY TRISELENIDE AND ANTIMONY TRITELLURIDE SEMICONDUCTORS

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Stoichiometrically adjusted antimony triselenide and antimony tritelluride semiconductors were carefully prepared for the first time. Numerous measurements were carried out, involving X-ray diffraction analysis, true density, thermogravimetric analysis and the temperature-dependence of the magnetic susceptibility. The results obtained indicated that antimony triselenide and antimony tritelluride polycrystals possess mass susceptibilities of -0.361×10^{-6} and -0.386×10^{-6} C.G.S., respectively. The results are discussed on the basis of electronegativity difference, partial ionicity of the bond, and bond strength.

Antimony triselenide and antimony tritelluride find useful application in the production of thermoelements, radars, transistors, diodes and rectifiers.

From an experimental point of view, it is not easy to prepare a semiconductor in standard form with special reference to those prepared from the molten state. This is because the susceptibility depends strongly on surface effects, particle size and firing temperature [1, 2]. Very little is known about the magnetic susceptibilities of antimony triselenide and antimony tritelluride semiconductors. As far as the author is aware, no mention is to be found in the literature concerning the dependence of the susceptibility of antimony triselenide and antimony tritelluride, giving values of -0.382 and -0.386×10^{-6} C.G.S. for antimony triselenide and antimony tritelluride, respectively. Following Matyas [3], various authors [4–6] studied the temperature-dependence of the magnetic susceptibility of antimony tritelluride from low temperature up to 1.3 K, using single and polycrystalline specimens.

The aim of the present work was to investigate the magnetic susceptibilities of pure stoichiometrically adjusted compounds at room and elevated temperatures in

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conjunction with earlier determined physical properties [7]. Previous papers reported studies of X-ray diffraction patterns, infrared absorption spectra and electrical conductivity for the same compounds [8–13].

Experimental

Material synthesis and sample preparation

The dry method used in the preparation of antimony triselenide was very similar to that given by Tideswell et al. [8], with some modification for adjust most of the stoichiometry of the compound obtained. The method applied in the preparation of antimony tritelluride was very similar to that reported by Black et al [9] The major modification involving the "re-Master Alloying Technique", i.e. master alloying several times until as stoichiometrically correct an ingot as possible was obtained.

Thus, the two compounds were prepared by a careful course of heat treatments, using the "Master Alloying" technique in order to attain as correct stoichiometry as possible for the materials prepared. This was followed by a special programme of chemical and spectral analyses, together with pycnometric density determination and Cu–K_α X-ray diffraction analysis.

Thermogravimetric analysis

The prepared and stoichiometrically corrected samples were subjected to thermogravimetric analysis with an automatic recording thermobalance. Measurements were made in the temperature range from 25° up to 500° in air.

Magnetic susceptibility measurements

Measurements of magnetic susceptibility were performed at room and elevated temperatures, using the Gouy method [12] with minor modification. Measurements of magnetic susceptibility at different applied magnetic fields indicated the absence of any ferromagnetic impurities for all samples investigated.

The mass susceptibility χ_s was calculated from the relation:

$$\chi_s = [(W/\mathrm{d}W)(\mathrm{d}S/S)]\,0.72\times 10^{-6} + 0.029\times 10^{-6}\,[1/\sigma - (W/\mathrm{d}W)(\mathrm{d}S/S)\times 1/d]$$

where dS is the net force resulting from the material, dW is the net force resulting from the reference material (redistilled water) and σ is the true density of the sample. This was determined pycnometrically in each case, using n-hexane as the immersion liquid. The values obtained were reproducible within the limits of experimental error (± 0.01 g/cm^3). Measurements were made on samples having a comparable average particle size. Correction for porosity was made using Krishnan's equation [11].

Results and discussion

From Table 2 it can readily be seen that the measured (present value) magnetic susceptibility of antimony triselenide is in good agreement with that given by Matyas [3]. Similarly, that obtained for antimony tritelluride is also in good agreement with that given by Matyas [15]. However the value given by Itterbeek et al. [5] is slightly different. This could be due to the differences in stoichiometry, impurity content, mode of preparation and previous history between various specimens.

Table 1 Measured and literature values of true densities (g/cm^3) of antimony triselenide and antimony tritelluride specimens at room temperature

Antimony triselenide		Antimony tritelluride	
Measured value	Literature values	Measured value	Literature values
5.8	5.84 [12] 5.93 [13]	6.57	6.51 [12] 6.48 [14]

Table 2 Values of diamagnetic susceptibility ($\times 10^{-6}$) of Sb_2Se_3 and Sb_2Te_3 specimens

Antimony triselenide		Antimony tritelluride	
Measured value	Literature value	Measured value	Literature values
0.361	0.382 [3]	0.386	0.398 [3] 0.383 [15] 0.314 [5]

The results of thermogravimetric analysis revealed that the triselenide and tritelluride did not undergo any weight change up to 300°. Thus, it seemed desirable to follow the variations in magnetic susceptibility as functions of temperature variation. Figures 1 and 2 show the variations in the magnetic susceptibilities of antimony triselenide and antimony tritelluride respectively as functions of temperature. It can clearly be seen that for both compounds the susceptibility is temperature-independent over the temperature range studied. This is due to the fact that the samples are completely free from impurities, or the impurity content is too

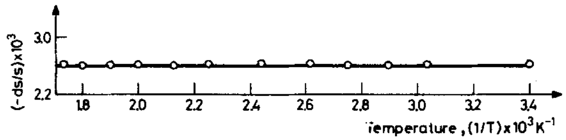

Fig. 1 Temperature dependence of magnetic susceptibility of antimony triselenide semiconductor

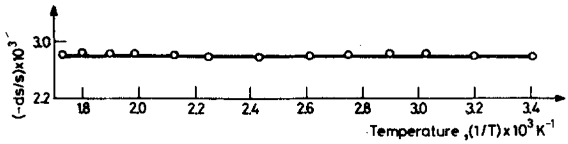

Fig. 2 Temperature dependence of magnetic susceptibility of antimony tritelluride semiconductor

small to influence the diamagnetic behaviour. This is in conformity with the results of chemical, X-ray, spectral analysis and conductivity measurements [4], which revealed that both compounds possesses minimal structure defects and impurity contents.

It is clear that there is an increase in the diamagnetic susceptibility on going from antimony triselenide to antimony tritelluride. This may be due to the decrease in bond strength in the same direction. The bond strength decreases as the electronegativity difference and partial ionic character decrease on going from antimony triselenide to antimony tritelluride.

Accordingly, our present results are all in conformity and the mass magnetic susceptibility (χ_s) values for materials stoichiometrically prepared by the "Master alloying technique" are evaluated here for the first time.

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Zusammenfassung — Stöchiometrische Antimontriselenid- und Antimontritellurid-Halbleiter wurden erstmals hergestellt. Zahlreiche Messungen wurden daran ausgeführt, und zwar Röntgendiffraktometrie, wahre Dichte, Thermogravimetrie und Temperaturabhängigkeit der magnetischen Susceptibilität. Die erhaltenen Ergebnisse zeigen, daß Polykristalle von Antimontriselenid und Antimontritellurid Massensusceptibilitäten von $-0.361 \cdot 10^{-6}$ bzw. $-0.386 \cdot 10^{-6}$ c.g.s. besitzen. Die erhaltenen Ergebnisse werden auf der Basis der Elektronegativitätsdifferenz, der partiellen Ionisierung und der Bindungsstärken diskutiert.

Резюме — Получены полупроводниковые триселенид- и трителлурид сурьмы со строго стехиометрическим составом. Проведен их рентгеноструктурный анализ, определение плотности, термогравиметрический анализ и температурная зависимость магнитной восприимчивости. Результаты показали, что поликристаллические образцы триселенида- и трителлурида сурьмы обладают магнитной восприимчивостью равной, соответственно, $-0{,}361 \cdot 10^{-6}$ и $-0{,}386 \cdot 10^{-6}$ СГС. Полученные результаты обсуждены на основе различной электроотрицательности халькогенидных атомов, частичной ионности связи и силы связи.