Pramana – J. Phys., Vol. 37, No. 2, August 1991, pp. 141–146. © Printed in India.

Electrical resistivity study on $SmSe_{1-x}As_x$ under pressure

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MS received 10 April 1991; revised 10 June 1991

Abstract. Electrical resistivity measurements under pressure and lattice parameter study on $SmSe_{1-x}As_x$ are reported here. The estimated lattice parameter and valence is calculated for the same and they are found to be in good agreement with the experimental data. The electrical conductivity increases with the increase of As concentration.

Keywords. $SmSe_{1-x}As_x$; lattice parameter; electrical resistivity.

PACS Nos 72·15; 61·55

1. Introduction

First order semiconductor to metal transition is observed in SmS under pressure at 6.5 kbar (Jayaraman *et al* 1970b) where there is a large decrease in the lattice parameter and a colour change from black to gold. Valence transition (Robinson 1979) is observed in SmS at ambient pressure and temperature by alloying with SmAs (Beeken and Schweitzer 1979) and SmP (Henry *et al* 1979). Dilute substitutions of As for the divalent S in SmS cause six neighbouring Sm ions to become trivalent but the extra electrons remain localized. As the arsenic concentration is increased, there is an abrupt transition to a homogeneous intermediate valence phase for the Sm ions, with electrons delocalized into the conduction band (Beeken and Schweitzer 1981). The first-order character in SmS distinguishes it from the continuous transitions observed in SmSe and SmTe (Bucher *et al* 1971). The problem of finding the reason for this difference in terms of physical parameters is still unresolved. With a view to provide some information about the effect of As substitution in SmSe for Se, electrical resistivity study has been carried out. This paper reports the lattice parameter and electrical resistivity measurements on $SmSe_{1-x}As_x$ under pressure.

2. Experimental methods

X-ray powder diffraction studies on $SmSe_{1-x}As_x$ for $x = 0{\cdot}1$ and $0{\cdot}4$ were carried out using MoK_α radiation produced by a rotating anode X-ray generator. The samples had expected NaCl type crystal structure.

Lattice parameters (table 1) obtained from nine d-values by least square method are in good agreement with the reported values (Beeken and Schweitzer 1981).

Electrical resistivity measurements were made by four-probe method (Victor Jaya 1988) in a Bridgeman anvil set-up, with anvils made of En24 (AISI 4340) alloy steel

Table 1. The d-spacings obtained from X-ray diffraction study.

$SmSe_{0.9}As_{0.1}$		$SmSe_{0.6}As_{0.4}$		SmAs (ASTM values) (File No: 10–39)	
d	hkl	d	hkl	d	hkl
1·04	600	0·99	600	0·99	600
1·10	440	1·05	440	1·04	440
1·26	422	1·21	422	1·21	422
1·39	420	1·34	420	1·32	420
1·55	400	1·49	400	1·48	400
1·82	311	1·77	311	1·79	311
2·22	220	2·11	220	2·09	220
3·12	200	3·05	200	2·96	200
3·64	111	3·36	111	3·41	111
		Lattice parameters Å			
Present study	Reported*	Present study	Reported*	The ASTM value (File No: 10–39)	
6·18 ± 0·02	6·15	5·94 ± 0·02	5·94	5·92	

*(Beeken and Schweitzer 1981)

(Composition: C – 0·40%, Mn – 0·6%, Ni – 1·55%, Cr – 1·1%) hardened to RC60. The anvil face was 10 mm in diameter and had a tapering angle of 10°. The pressure medium was steatite of 0·2 mm dia. The gaskets were pyrophyllite discs of 10 mm dia. A hydraulic press was used to apply the force.

3. Estimated lattice parameter and room temperature valence

SmSe crystallizes in the NaCl type structure with a lattice constant of 6·20 Å and is a semiconductor. The lattice parameter of $SmSe_{1-x}As_x$ is found to decrease with increasing As concentration as shown in table 1.

The electronic properties of samarium pnictides SmP, SmAs and SmSb are similar with all of the compounds showing semimetallic behaviour. For $SmS_{1-x}As_x$ alloys, lattice constant, magnetization, resistivity and Hall constant measurements are consistent with the presence of both $Sm^{2+}(4f^6)$ and $Sm^{3+}(4f^5)$ ions, where Sm ions with one or more As as nearest neighbours are trivalent as originally suggested by Kasuya (Henry *et al* 1979). If the same principle is applied to $SmSe_{1-x}As_x$ alloys, the expected lattice parameter can be estimated from linear interpolation which gives

$$a(x) = [1 - x - (1-x)^6]a(Sm^{3+}Se) + (1-x)^6 a(Sm^{2+}Se) + xa(SmAs) \quad (1)$$

where $(1-x)^6$ is the probability that a Sm ion has no As ions at nearest neighbour sites, a(SmAs) is the lattice parameter of SmAs, $a(Sm^{2+}Se)$ is the measured lattice parameter of SmSe and $a(Sm^{3+}Se) = 5{\cdot}84$ Å is an estimated value based on an interpolation from the lattice parameter of the neighbouring trivalent rare earth

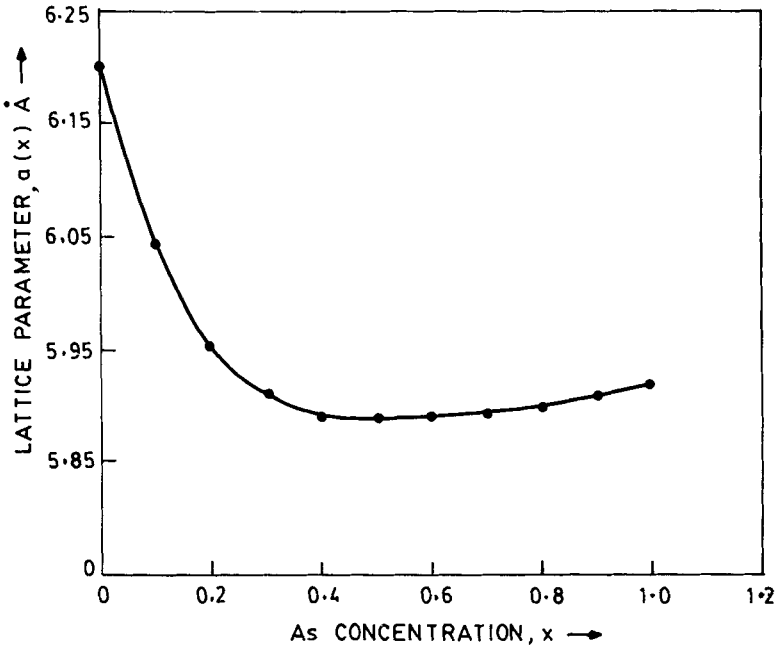

Figure 1. Estimated lattice parameter as a function of As concentration in $SmSe_{1-x}As_x$.

selenides. The calculated lattice parameters using (1) are in good agreement with the reported values (Beeken and Schweitzer 1981). Estimated lattice parameter as a function of As concentration is shown in figure 1.

The lattice parameters were used to estimate the Sm valence at a given composition assuming a model of hard sphere (Pollak *et al* 1974). An estimate of Sm valence $v(x)$ is given by

$$v(x) = 2 + x + \frac{(1-x)a(Sm^{2+}Se) + xa(SmAs) - a(x)}{a(Sm^{2+}Se) - a(Sm^{3+}Se)} \tag{2}$$

where $a(x)$ is the lattice parameter of the alloy. The resulting estimate for the Sm valence using (2) as a function of arsenic concentration is shown in figure 2. The estimated lattice parameters and valence for various As concentrations are given in table 2.

4. Electrical resistivity study

A continuous pressure induced semiconductor to metal transition has been reported in SmSe and SmTe (Jayaraman *et al* 1970a) from electrical resistivity measurements. We have also studied the effect of As substitution in SmSe for Se on the pressure dependence of electrical resistivity. Since, the valence transition starts at $x = 0{\cdot}1$ and is nearly complete at about $x = 0{\cdot}4$, we have studied the electrical resistivity behaviour for these two As concentration (figure 3). We also examined the semiconductor to metal transition by probing the change in the sign of the temperature coefficient of resistivity, and the magnitude of resistivity. At ambient temperature and pressure, for $x = 0{\cdot}1$

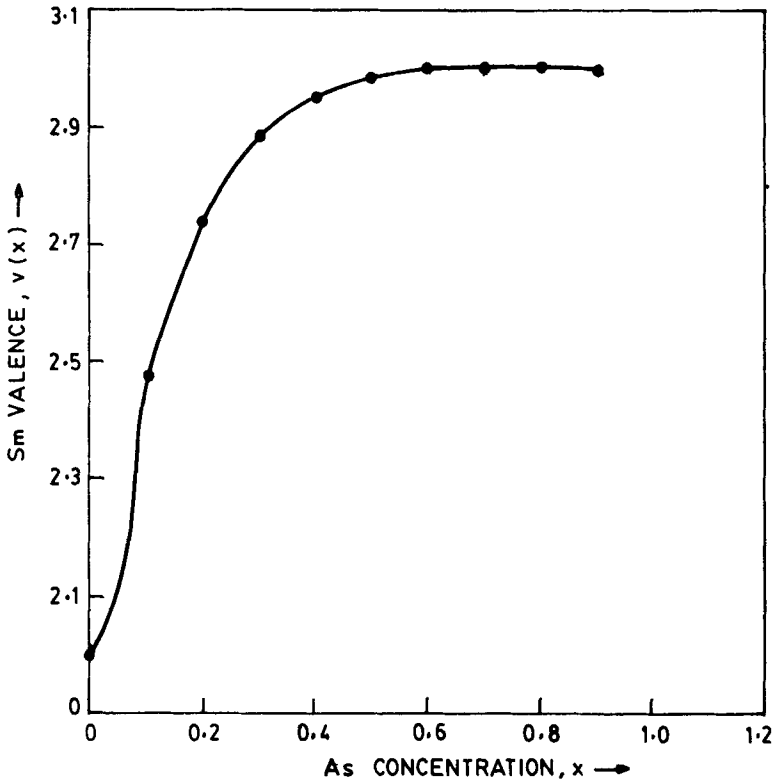

Figure 2. Samarium valence as a function of As concentration in $SmSe_{1-x}As_x$.

Table 2. Estimated lattice parameter $a(x)$ and samarium valence $v(x)$ for various As concentration x in $SmSe_{1-x}As_x$.

x	$a(x)$ Å	$v(x)$
0·1	6·20	2·00
0·1	6·04	2·47
0·2	5·95	2·74
0·3	5·91	2·88
0·4	5·89	2·95
0·5	5·89	2·98
0·6	5·89	3·00
0·7	5·90	3·00
0·8	5·90	3·00
0·9	5·91	3·00
1·0	5·92	3·00

and 0·4, the electrical resistivity (ρ) is found to be $1{\cdot}2 \times 10^{-2}\,\Omega$m and $0{\cdot}1 \times 10^{-3}\,\Omega$m respectively. At a pressure of about 60 kbar, ρ is found to be $2 \times 10^{-2}\,\Omega$m and $1{\cdot}6 \times 10^{-5}\,\Omega$m respectively. The electrical conductivity of $SmSe_{1-x}As_x$ is found to increase with As substitution by an order of magnitude, even at room temperature. The temperature coefficient of resistivity is nevertheless negative like that of a

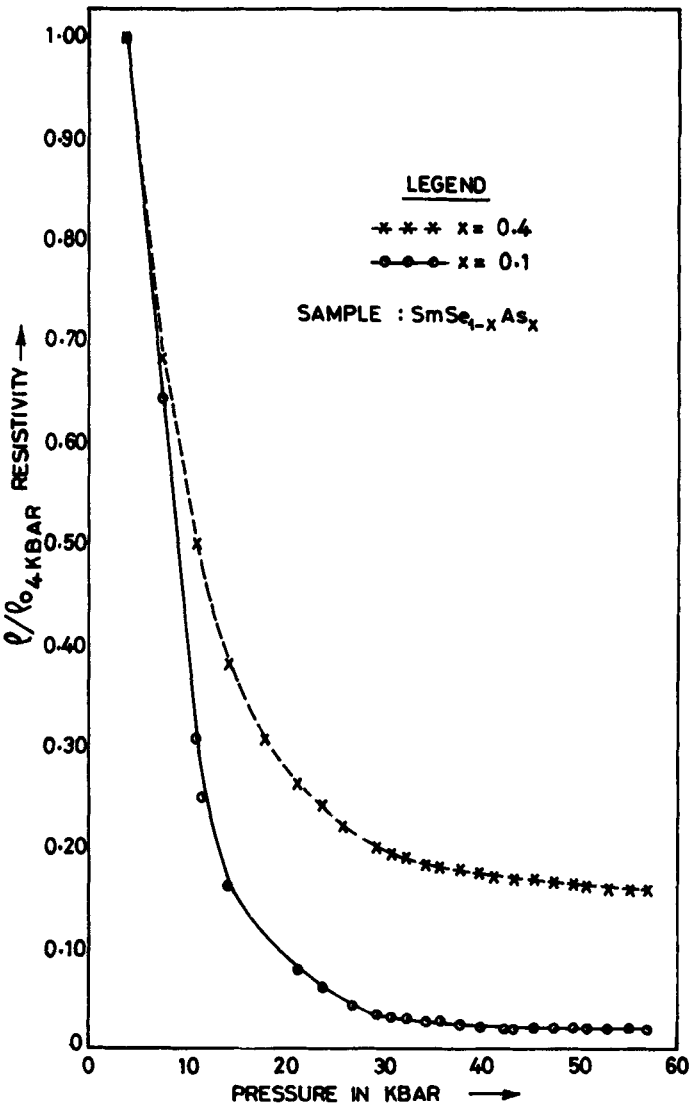

Figure 3. Normalized resistivity versus pressure for $SmSe_{1-x}As_x$.

semiconductor but it changes to metallic behaviour under pressure. It is reported that SmSe and SmAs are semiconductor and semimetal respectively (Jayaraman and Maines 1979).

5. Conclusion

The estimated lattice parameters of $SmSe_{1-x}As_x$ are in good agreement with the measured values. Substitution of As in SmSe for Se causes the valence transition from Sm^{2+} to Sm^{3+}. This transition starts at about $x = 0{\cdot}1$ and is nearly complete at about $x = 0{\cdot}4$. The d-spacings obtained from X-ray powder diffraction studies for $SmSe_{0{\cdot}9}As_{0{\cdot}1}$ and $SmSe_{0{\cdot}6}As_{0{\cdot}4}$ are given in table 1. The d-values obtained for

$SmSe_{0.6}As_{0.4}$ agrees with the ASTM d-values of SmAs as shown in table 1. The electrical resistivity (ρ) of both the samples (figure 3) decrease with the pressure. Also decreases with increase in As concentration at room temperature but the temperature coefficient of resistivity is found to be positive, like that of the semiconductor. At high pressure, the sample exhibits metallic behaviour. These results lead to a conclusion that alloying SmSe with SmAs increases the electrical conductivity even at room temperature. And the sample $SmSe_{1-x}As_x$ is seen to behave like a semimetal at low pressure and metal at high pressure.

From the results, it is clear that the increase in As concentration causes Sm^{2+} to Sm^{3+} transition and reduces the excitation energy gap. The resistivity data shows that the transition is continuous (Jayaraman *et al* 1970a). The nature of transition can be explained in terms of excitation energy gap. Samarium chalcogenides such as SmSe and SmS are semiconductors with similar electronic structures. The excitation gap is larger for SmSe and smaller for SmS. It is reported that the excitation energies for SmSe and SmS are 0·46 eV and 0·06 to 0·25 eV respectively (Beeken and Schweitzer 1981). Larger excitation gap implies that the Sm is present in more stable divalent configuration and leads to continuous transition. The smaller excitation gap implies less stable divalent Sm configuration and leads to discontinuous transition.

Acknowledgements

We wish to thank Prof. K B Garg for providing the samples for this study and DST, Government of India for funding.

References

Bucher E, Narayanamurti V and Jayaraman A 1971 *J. Appl. Phys.* **42** 1741
Beeken R B and Schweitzer J W 1979 *Phys. Rev.* **B19** 5810
Beeken R B and Schweitzer J W 1981 *Phys. Rev.* **B23** 3620
Henry D C, Sisson K J, Savage W R and Schweitzer J W 1979 *Phys. Rev.* **B20** 1985
Jayaraman A, Narayanamurti V, Bucher E and Maines R G 1970a *Phys. Rev. Lett.* **25** 368
Jayaraman A, Narayanamurti V, Bucher E and Maines R G 1970b *Phys. Rev. Lett.* **25** 1430
Jayaraman A and Maines R G 1979 *Phys. Rev.* **B19** 4154
Pollak R A, Holzberg F, Freeouf J L and Eastman D E 1974 *Phys. Rev. Lett.* **33** 820
Robinson J M 1979 *Phys. Rep.* **51** 1
Victor Jaya N 1988 *High pressure studies of quasicrystals and superconducting compounds* Ph.D thesis Anna University