Electronic Properties of $Co_{1-x}Sb_x$

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Abstract- Thermo-power and magnetization measurements of $Co_{1-x}Sb_x$ (0<x<0.5) are presented here. The estimation of Fermi energy, energy of d-band edge and density of states using Kolomoets' two band model indicates that the electronic structure of the alloys may be described by cobalt 3d bands overlapping broader antimony p bands. The Fermi level is located slightly below the d-band edge. On increasing antimony, the Fermi level and d-band edge shifts to high energy side filling the d-band and causing a decrease in magnetic moment.

Index Terms- Thermo-power; Fermi Energy; Density of states; Magnetic Moments.

I. INTRODUCTION

Properties such as resistivity, thermoelectricity of transition metals, intermetallic compounds have been studied earlier [1,2,3]. Magnetic properties of bulk amorphous alloys are also studied extensively. Soft magnetic metallic glasses have wide variety of applications such as position sensor, solenoid valves, magnetic sensor etc.[4].

Studies of thermoelectricity in metals, alloys and semiconductors yield information about electronic structure and about the interactions between electrons and both lattice vibrations and impurities. Their practical applications include the measurement of temperature, generation of power, cooling and heating etc.[5].

Thermo-power S, is sensitive to many factors. The addition of impurities can change the thermo-power of pure metal [6]. In a non-cubic material [7], two samples from such a non-cubic crystal cut in different directions may be thermoelectrically different even if each sample is highly homogeneous. Thermo-power also depends on electron diffusion, phonon drag and magnon drag effects.

In case of pure metals and alloys, it is observed that phonon drag and magnon drag effects are prominent at Debye temperatures much lower than room temperature. Above room temperature, their influence over the thermo-power is negligible and only the electron diffusion component plays an important role [8].

Thermoelectric properties of many magnetic metals have been reported [9,10]. For pure cobalt it is observed that the crystal structure hcp or fcc is not an important parameter in determining S. It is of greater interest to note that the S Vs T curve goes through a very deep minimum at 600K and then abruptly changes slope near the Curie point [10]. The value of S remains negative in the temperature range 0-1200K.

Metallic glasses prepared from transition ferromagnetic metal and metalloid such as $Co_{1-x}B_x$, $Co_{1-x}P_x$ etc. [11,12,13] have been extensively investigated for their importance. We report here thermoelectric properties of $Co_{1-x}Sb_x$ alloys where x = 0.17, 0.25, 0.33, 0.36, 0.40 and 0.44.

II. EXPERIMENTAL

The samples of $Co_{1-x}Sb_x$ were synthesized by first preparing CoSb in induction furnace and annealing. Then cobalt was added to it in appropriate weight proportion and again melted in induction furnace. The samples then were again annealed.

To confirm the formation of $Co_{1-x}Sb_x$ samples produced by above mentioned CoSb route, XRD patterns were obtained by using the D500 Siemens, Germany and the Rigaku, Japan diffractometers (both use Copper target).

A flat sample held between two platinum electrodes is sandwiched between two spring-loaded copper rods. These copper rods are insulated electrically from the sample by inserting mica sheets between the rods and the platinum electrodes. Further the rods are heated unequally by two identical furnaces to ensure a constant temperature difference adjustable between 5K and 10K and the average temperature of the sample variable from room temperature to about 600K.

III. RESULT

The XRD patterns of all the samples $Co_{1-x}Sb_x$ were obtained using $K\alpha_1$ and $K\alpha_2$ (λ_1 = 1.54051Å and λ_2 = 1.54433Å respectively) emission lines of copper. The inter-planer distance 'd' and the relative intensities corresponding to all samples of $Co_{1-x}Sb_x$ are listed in Table 1 and 2.

All the thermo-power measurements ($S_d, \mu V/K$) have been carried out between room temperature and 510K (Fig.1). It is observed that thermo-power is negative for all the samples at all the temperatures (T). All the S_d Vs T curves, except the one corresponding to x = 0.36, exhibit a change in the sign of slope between room temperature and 350K. It indicates that some kind of order-disorder transition has already occurred. This transition is certainly not due to ferromagnetic to paramagnetic or hcp to fcc transitions which occur at 1100K and 700K in case of cobalt.

Also since S_d is not proportional to 1/T after transition, it is not a phonon drag effect [14]. Possibly it is due to spin orbit scattering, electron-electron scattering or magnon drag [15].

In the range $0.17 \leq x \leq 0.33$, this transition is followed by a linear portion between 350K and 450K and as x increases the slope decreases. Above 450K these curves become nonlinear. Corresponding to x = 0.40 and 0.44 the curves are nonlinear and rather steep between 350K and 500K. In the case of sample with x = 0.36, this transition is missing and the curve is almost flat and nonlinear.

Table 1: Miller Indices (hkl), Intensities (I/I_0) and Inter-planar distances (d) (observed and calculated) corresponding to system $Co_{1-x}Sb_x$ (x = 0.17, 0.20, 0.25, 0.33).

	X = 0.17			X = 0.20			X = 0.25			X = 0.33		
hkl	I/I_0	dobs	dcal	I/I_0	dobs	dcal	I/I_0	dobs	Dcal	I/I_0	dobs	dcal
101	100	2.816	2.816	100	2.842	2.841	100	2.839	2.839	100	2.879	2.879
002	91	2.041	2.036	19	2.598	2.595	-	-	-	11	2.611	2.624
102	81	1.949	1.949	49	2.061	2.061	79	2.061	2.056	60	2.077	2.087
110				43	1.961	1.961	63	1.962	1.963	40	1.988	1.988
201				14	1.617	1.614	-	-	-	12	1.635	1.636
112				-	-	-	-	-	-	7	1.580	1.585
103				16	1.539	1.542	40	1.539	1.536	13	1.548	1.560
202				15	1.422	1.421	34	1.461	1.419	11	1.434	1.439
113							35	1.295	1.294	-	-	-
210							-	-	-	-	-	-
211							38	1.248	1.246	9	1.261	1.263
104							-	-		5	1.221	1.219

Table 2: Miller Indices (hkl), Intensities (I/I_0) and Inter-planar distances (d)(observed and calculated) corresponding to system $Co_{1-x}Sb_x$ (x = 0.36, 0.40, 0.44).

	X = 0.36			**X = 0.40**			**X = 0.44**		
hkl	**I/I_0**	**dobs**	**dcal**	**I/I_0**	**dobs**	**Dcal**	**I/I_0**	**dobs**	**Dcal**
101	**100**	**2.847**	**2.847**	**100**	**2.852**	**2.852**	**100**	**2.855**	**2.854**
002	**8**	**2.598**	**2.601**	**5**	**2.602**	**2.607**	**8**	**2.602**	**2.606**
102	**65**	**2.062**	**2.066**	**52**	**2.066**	**2.070**	**64**	**2.068**	**2.071**
110	**52**	**1.964**	**1.964**	**46**	**1.967**	**1.967**	**45**	**1.969**	**1.969**
201	**17**	**1.617**	**1.617**	**19**	**1.618**	**1.618**	**17**	**1.620**	**1.621**
112	**11**	**1.566**	**1.567**	**7**	**1.567**	**1.567**	**10**	**1.568**	**1.571**
103	**18**	**1.541**	**1.544**	**17**	**1.543**	**1.543**	**18**	**1.544**	**1.548**
202	**16**	**1.421**	**1.423**	**17**	**1.423**	**1.423**	**13**	**1.425**	**1.427**
113				**20**	**1.296**	**1.296**	**5**	**1.297**	**1.303**
210				**8**	**1.293**	**1.293**	**-**	**-**	**-**
211				**13**	**1.248**	**1.248**	**13**	**1.249**	**1.251**
104				**10**	**1.213**	**1.213**	**7**	**1.215**	**1.217**

The magnetic measurements of these samples between room temperature and 600K indicate constant magnetic moments. Hence magnetic moments computed at room temperature are listed in Table 3 to facilitate the comparison. It is observed that except for x =0.20 the magnetic moment decreases linearly as x increases (Fig. 2).

I. DISCUSSION

The electronic structure of transition metals, particularly Fe, Co and Ni is determined by the electronic population of overlapping 4s and 3d bands. Further, the Fermi level in these metals is near, yet below the top of the density of states curve for the d band. Therefore, the electronic structure of Co-Sb alloys may be described in terms of 4s and 3d bands, the overlapping of which is influenced by a broader antimony p band. The Fermi level in these alloys should lie near the top of d band as in cobalt and CoSb [16]. On the basis of band theory, the negative sign of the thermo-power as observed by us indicates the presence of holes i.e. more than half filled band [17]. Further the magnetic moments in all our samples are less than that in cobalt. This too implies that the d band is almost full is applicable here.

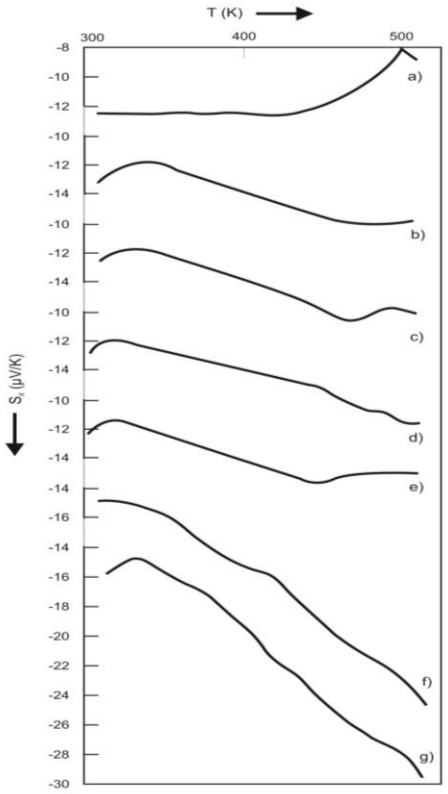

Figure 1: Thermopower S_d (μV/K) Vs absolute temperature T (K) corresponding to $Co_{1-x}Sb_x$.
a) x = 0.36, b) x = 0.33, c) x = 0.17, d) x = 0.20, e) x = 0.25, f) x = 0.44, g) x = 0.40.

Table 3:Magnetic moment, Fermi Energy, Top of the d-band and Density of states corresponding to $Co_{1-x}Sb_x$.

X	$E_F(eV)$ (±0.02eV)	$E_d(eV)$ (±0.02eV)	$N_d(E_F)$ (states/eV unit cell at 400K)	Magnetic moment (μ_B) (±0.05μ_B)
0.17	1.06	1.11	1140	1.25
0.20	1.08	1.13	1150	1.35
0.25	1.10	1.15	1130	1.05
0.33	1.12	1.17	1170	0.70
0.36	1.14	1.18	930	0.50
0.40	1.16	1.19	1880	0.45
0.44	1.18	1.21	1800	0.15

If the thermo-power is free from all transitional effects then the electron diffusion thermo-power S_d at temperature T using a two band model is given by [5,15].

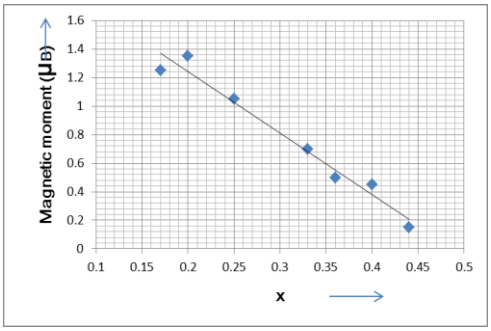

Figure 2: Magnetic Moment μ_BVs x in $Co_{1-x}Sb_x$

$$S_d = -\frac{\pi^2 K^2 T}{3|e|}\left[\frac{3}{2E_F} - \frac{1}{N_d(E)}\cdot\frac{dN_d(E)}{dE}\right] \text{ at } E = E_F \quad \text{-- (1)}$$

Where E_F = Fermi energy, $N_d(E)$ = density of states of d electrons at energy E.

If the $N_d(E)$ Vs E curve has a minimum or maximum or if $N_d(E)$ is independent of E in the vicinity of the Fermi energy then

$$\frac{1}{N_d(E)}\cdot\frac{dN_d(E)}{dE} \ll \frac{3}{2E_F}$$

we get

$$E_F = -\frac{\pi^2 K^2 T}{2S_d|e|}$$

i.e. $$S_d = \frac{-\pi^2 K^2}{2|e|E_F}T$$

Since Fermi energy in metals and alloys is weakly dependent on temperature, a plot of S_d Vs T should be a straight line passing through origin. If the initial nonlinear transitional portion of the curve is ignored then the linear portion in the temperature range 350K ≤ T ≤ 450K is indeed a straight line which passes through origin after extrapolation in cases where (0.17 ≤ x ≤ 0.33). The Fermi energies computed from the slope are listed in Table 3. They are of the same order as reported for 3d metals [18,19,20] and are observed to increase as the content of antimony is increased. This is indicative of continuous filling of d bands. Also the decreasing magnetic moment (except for x = 0.20) indicates the continuous filling of d band as the content of antimony increases. The exception for x=0.20 may be due to the increase in the difference between spin up and spin down densities of states near Fermi energy.

For x > 0.36, the linear portions of S_d Vs T curves do not pass through the origin when extrapolated. This means

$$\frac{1}{N_d(E)}\cdot\frac{dN_d(E)}{dE}$$

is large and temperature dependent. This would happen where $N_d(E_F)$ changes rapidly even for small changes in Fermi energy. Hence it is difficult to compute directly the Fermi energies corresponding to these samples. However a linear relationship is observed between Fermi energies and x (Fig.3) corresponding to 0.17 ≤ x ≤ 0.33. Hence extrapolating this line the Fermi energies corresponding to 0.36 ≤ x ≤ 0.44 are estimated. These values are also indicated in Table 3. These Fermi energies are substituted in equation (1) and the densities of states are calculated at 400K and are also reproduced in Table 3. It is observed that N_d is nearly constant in 0.17 ≤ x ≤ 0.36 and rises rapidly for x = 0.40 and x = 0.44 (Fig.4)

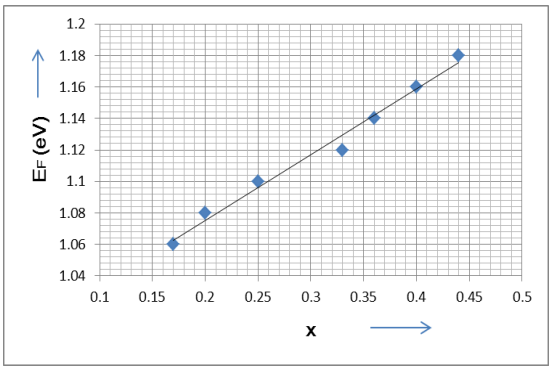

Figure 3: Fermi Energy E_FVs x in $Co_{1-x}Sb_x$

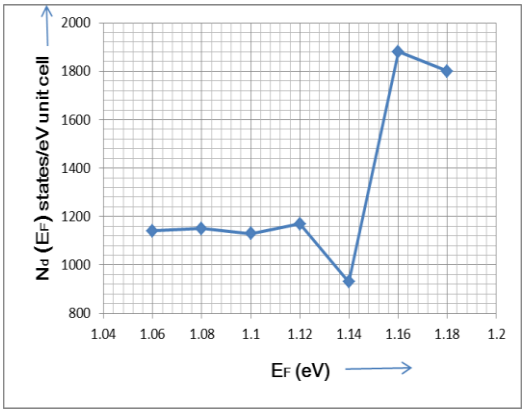

Figure 4: Density Of States of $Co_{1-x}Sb_x$ near Fermi Energy

The gross features of the density corresponding to similar alloys of 3d metals are of same order [19,21]. Our densities of states at different Fermi energies are near the top of the d band. They are compared with the density of states curve for CoAs [22] near top of the d band. It is interesting to note that in both the cases N_d rises sharply.

It is possible to calculate E_d using S_d Vs γ curve [20] where E_d is d band edge closest to Fermi level and $\gamma = (E_d - E_F)/kT$. Values of E_d calculated in this manner are reproduced in Table 3. It is observed that $E_d > E_F$ and E_d increases with the contents of antimony. However $(E_d - E_F)$ decreases with increasing Sb content indicating filling of d band and reduction in magnetic moment. This observation is consistent with magnetic measurements.

II. CONCLUSION

The increasing antimony in Co-Sb alloys shifts the Fermi level (E_F) and d band edge (E_d) to high energy side where $E_d > E_F$. However $(E_d - E_F)$ decreases with increasing Sb content. This causes a rapid decrease in magnetic moment and

rapid increase in density of states near Fermi level for x>0.36.

REFERENCES

[1] Okram G. S., 2012, AIP Advances 2, 012178.
[2] Soni A., Okram G. S., 2008, Rev. Sci. Instru., 79, 125103.
[3] Cook B.A. and Harringa J.L., 1999, J. Mat. Sci. 34, p 323-327.
[4] Inoue A. and Nishiyama N., 2007, MRS Bulletin, vol. 32(08), p 651.
[5] Bass Jack, 1988, 'Solid State Physics Source Book', ed. Sybil Parkar, McGraw Hill, Singapore, p165.
[6] Crisp R. S. and Rungis J., 1970, Phil Mag. 22, p 217.
[7] Rowe V.A. and Schroeder P. A., 1970 J. Phys. Chem. Sol. 31, p1.
[8] Chen Tu, Rogowski D. and White R. M., 1978 J. Appl. Phys.49, p1425.
[9] Mori Takao, 2011, Boron Rich Solids, ed. Nina Orlovskaya and Mykola Lugovy, Springer Netherlands, pg 63-81
[10] Vedernikov M. V., 1969, Adv. Phys. 18, p 337.
[11] Corb B. W., O'Handley R. C., Grant N. J., 1983, Phys. Rev. B27, p636.
[12] Iskhakov R. S., Popov G. V. and Karpenko M. M., 1983, Phys. Met. Metall, 56, p 636.
[13] Waseda Y. and Chen H.S., 1978, Physica Status Solidi (a), 49(1), p 387.
[14] Mac Donald D. K. C., 1961, Thermoelecricity: an introduction to the principles, John Willy and Sons, New York, p. 23.
[15] Blatt F. J., 1972, Can. J. Phys. 50, p 2836.
[16] Tilley R., 2004, Understanding Solids: The Science of materials, John Willy and sons, England, p 382.
[17] Patki M. S. and Salvi S. V., 1991, SSP Symposium Proc. Vol. 34C, p96.
[18] Kolomoets N. V., 1966, Fig. Tverd (Sov. Phys. Solid State) 8, p 799.
[19] Koster G. F., 1955, Phys. Rev. 98, p 901.
[20] Langlinais J. and Callaway J., 1972, Phys. Rev. B5, p 124.
[21] Cyrot M. et Lavagna M., 1979, J.Phys. France, vol. 40(8), p763.
[22] Morifuji M. and Motizuki, 1987, J. Magn. Magn. Mat. 70, p 70.

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