Atomic and magnetic order in the weak ferromagnet CoVSb: is it a half-metallic ferromagnet?

2005 J. Phys.: Condens. Matter 17 4991

(http://iopscience.iop.org/0953-8984/17/33/004)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **17** (2005) 4991–4999 doi:10.1088/0953-8984/17/33/004

Atomic and magnetic order in the weak ferromagnet CoVSb: is it a half-metallic ferromagnet?

L Heyne[1], T Igarashi[2], T Kanomata[2], K-U Neumann[1], B Ouladdiaf[3] and K R A Ziebeck[1]

[1] Physics Department, Loughborough University, Leicester LE11 3TU, UK
[2] Faculty of Engineering, Tohoku Gakuin University, Tagajo 985-8537, Japan
[3] Institut Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France

Received 9 May 2005, in final form 17 June 2005
Published 5 August 2005
Online at stacks.iop.org/JPhysCM/17/4991

Abstract

Magnetization and neutron powder diffraction measurements have been carried out on CoVSb. Both the transport and magnetic properties are predicted by band theory to depend upon the nature of the atomic order in the $C1_b$ lattice. Calculations in which the cobalt atoms occupy the (4b) site predict half-metallic behaviour and a ground state moment of $\sim$1 μ_B per formula unit with 1.19 μ_B on the vanadium atoms and -0.19 μ_B on the cobalt atoms. However, calculations in which the Sb or V atoms occupy the (4b) site predict larger moments, $\sim$0.7 μ_B, on the cobalt atoms, and either zero or a negative moment on the vanadium atoms. In contrast, the magnetization measured in fields of up to 5.5 T is small, amounting to a ferromagnetic moment per formula unit of 0.17 μ_B at 2 K. Both the field dependence of the magnetization in the ordered phase below $T_c \sim 48$ K and the large effective moment obtained from the Curie–Weiss susceptibility above T_c are consistent with weak itinerant ferromagnetism. Confirmation of the small ground state moment and hence the absence of any significant moment on the vanadium atoms was obtained from neutron powder diffraction measurements, which also enabled the crystallographic structure to be determined as $C1_b$ with the cobalt atoms occupying the (4b) sites. The results show that CoVSb is not a half-metallic ferromagnet as predicted by band theory.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The possibility of using the electronic spin degree of freedom in new semiconductor devices, e.g. spin valves, to increase giant magneto-resistance (GMR) [1], as possible spin injector electrodes in tunnel magneto-resistance (TMR) structures [2, 3] or for spin polarized current injection into semiconductors (spintronics) is currently attracting considerable attention [4].

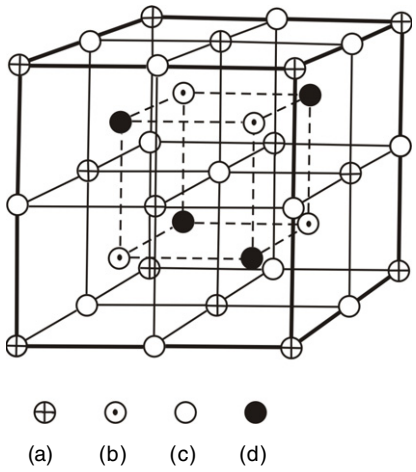

Figure 1. The $C1_b$ unit cell with space group $F\bar{4}3m$ comprising four interpenetrating fcc sublattices a (000), b ($\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$), c ($\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$) and d ($\frac{3}{4}\ \frac{3}{4}\ \frac{3}{4}$). All sites have $\bar{4}3m$ symmetry. The three different atomic arrangements for the $C1_b$ lattice considered in the band structure calculations listed in table 1 are

atomic order	site occupancy			
	a	b	c	d
CoVSb	Sb	Co	V	Void
SbVCo	Co	Sb	V	Void
VCoSb	Sb	V	Co	Void

Such devices require the injection of a spin polarized current and therefore substantial effort is being made to find suitable materials capable of providing these currents. Band structure calculations predict that some ferromagnetic compounds, Co_2MnSi [5], NiMnSb [6], CoS_2 [7], CrO_2 [8] etc, have half-metallic properties and hence are a potential source of spin polarized electrical currents. This prediction is based on there only being one spin sub-band at the Fermi level [6]. The other sub-band is either completely full and below the Fermi level or completely empty and above. Thus the electrical current arising from electrons near the Fermi surface will have one spin polarization. The problem of injection into the semiconductor is then one of conductance matching, which places additional constraints on material selection.

Half-metallic ferromagnetism was first predicted [6] in NiMnSb, which has the non-centrosymmetric $C1_b$ structure with space group $F\bar{4}3m$ shown in figure 1. From this figure it may be seen that the crystallographic structure is similar to that observed for Heusler $L2_1$ except that the ($\frac{3}{4}\ \frac{3}{4}\ \frac{3}{4}$) (4d) site is unoccupied. Since the first prediction of half-metallic ferromagnetism a considerable amount of work has been carried out on isostructural compounds by varying the components XYZ but as yet no ideal system has been found. More recently, it has been suggested that when ordered in the $C1_b$ structure with the cobalt atoms occupying the (4b) sites CoVSb is also a half-metallic ferromagnet with the majority of the moment $\sim 1\ \mu_B$ localized on the vanadium atoms. A vanadium moment of $\sim 1\ \mu_B$ in an intermetallic compound is unusual and therefore in itself merits experimental investigation. However, these calculations also show that the magnetic and transport properties depend sensitively on the type of atomic order, i.e. on which of the three atoms occupies the (4b) site. The results of these calculations are summarized in table 1.

Since the neutron scattering lengths are significantly different for the three elements Co, V and Sb, namely 2.5, −0.5 and 5.4 fm respectively, neutron diffraction is ideally suited to

Table 1. A summary of the results of band structure calculations for CoVSb.

Atomic order	Electrical	Co (μ_B)	V (μ_B)	Sb (μ_B)	Total (μ_B)	Reference
SbCoV	Metal	0.69	0.01	—	0.7	[9]
VCoSb	Metal	0.79	0.38	—	0.41	[9]
CoVSb	Halfmetal	−0.19	1.19	—	1.0	[9]
CoVSb	Halfmetal	−0.02	1.03	−0.03	0.98	[10]
CoVSb	Halfmetal	−0.126	1.074	−0.021	0.965	[11]
CoVSb	Halfmetal	−0.073	1.065	−0.021	0.985	[12]

determine the crystallographic structure and the moment distribution in CoVSb. A neutron powder diffraction investigation of CoVSb underpinned by magnetization measurements was therefore undertaken.

2. Experimental details

2.1. Sample preparation

A 10 g sample of CoVSb was prepared by solid state reaction of constituent elements of 99.99% purity. Using a ceramic pestle and mortar the starting elements in powder form were ground together in the ideal ratio 1:1:1. The resulting powder was pressed into pellets and sealed in an evacuated silica tube. After annealing at 650 °C for six days the specimen was quenched into ice water. The pellets were then reground and the powder subjected to a further anneal for five days, this time at 850 °C, before being again quenched into ice water. X-ray powder diffraction measurements using Cu Kα radiation indicated that the resultant powder had an fcc structure with a lattice parameter of 5.796 Å, close to that reported for the $C1_b$ structure [13].

2.2. Magnetization measurements

Magnetization measurements were made using a SQUID magnetometer in fields up to 5.5 T and at closely spaced temperatures between 5 and 350 K. The magnetization measured at 5 K is presented in figure 2 in the form of a hysteresis loop. The low spontaneous magnetization indicative of weak ferromagnetism is further demonstrated by the small hysteresis shown as an inset to figure 2. The spontaneous magnetization at 2 K leads to a magnetic moment per formula unit of 0.17 μ_B. From figure 2 it may be seen that the magnetization does not saturate in fields up to 5.5 T; the differential susceptibility $\left(\frac{\partial M}{\partial B}\right)_{HF} = 0.077$ J T^{-2} kg^{-1}. The magnetic isotherms were analysed in the form of Arrott plots (M^2 versus B/M) presented in figure 3, which enabled the thermal variation of the spontaneous magnetization, the Curie temperature T_c and the thermal dependence of the inverse susceptibility above T_c to be established. The thermal variation of the spontaneous magnetization, as obtained from the high field part of the Arrott plots, is shown as an inset to figure 4. The data are plotted in reduced form with the solid line representing a fit to the data using $M_{Arr}(T) = M_{Arr}\ (T = 0)\sqrt{\frac{T_c^* - T}{T_c^*}}$ as suggested by a simple mean field model [14]. T_c^* was refined to be 48.31 ± 0.83 K in close agreement with the value of the Curie temperature obtained from the Arrott plots. The thermal variation of the inverse susceptibility shown in figure 4 follows the form expected for Curie–Weiss behaviour with an effective moment of $\mu_{eff} = 1.34\ \mu_B$ per formula unit and a paramagnetic Curie temperature of 53.10 ± 1.5 K. Using $\mu_{eff}^2 = \mu_p(\mu_p + 2)$ a paramagnetic moment μ_p (gS) of 0.67 μ_B per formula unit was obtained. A summary of the magnetic results is given in table 2.

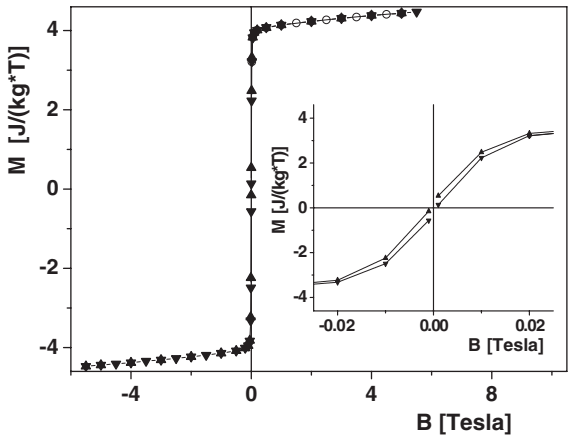

Figure 2. Magnetization of CoVSb at 5 K. The inset shows the small hysteresis.

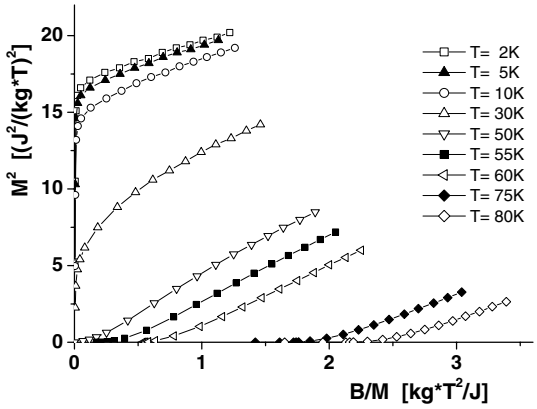

Figure 3. Magnetic isotherms of CoVSb in the form of Arrott plots.

Table 2. Magnetic properties of CoVSb.

T_C (K)	μ_{00}/fu (μ_B)	C (J K kg^{-1} T^{-2})	μ_{eff}/fu (μ_B)	μ_P/fu (μ_B)	Θ_P (K)
48 ± 1	0.17 ± 0.01	(9.83 ± 0.07)	1.35 ± 0.01	0.68 ± 0.01	53.1 ± 1.0

2.3. Neutron measurements

Neutron powder diffraction patterns were obtained at three temperatures, 2, 50 and 100 K, using the high resolution neutron diffractometer D1A at the ILL in Grenoble. Using a neutron wavelength of 1.911 Å, measurements were made for 2-theta values between 5° and 157° in steps of 0.05°. The powder was contained in a thin walled vanadium tube of diameter 5 mm located in an 'orange' ILL cryostat capable of providing temperatures stable to ±0.2 K over the required range. The diffraction patterns were analysed using the profile refinement technique as provided by the FullProf suite of programmes [15]. A statistical χ^2 test was used to measure

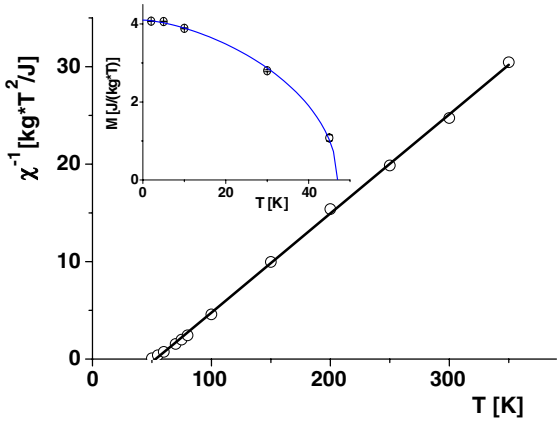

Figure 4. The thermal variation of the uniform inverse susceptibility of CoVSb. The inset shows the temperature dependence of the spontaneous magnetization below T_c with the solid line representing a mean field variation described in the text.

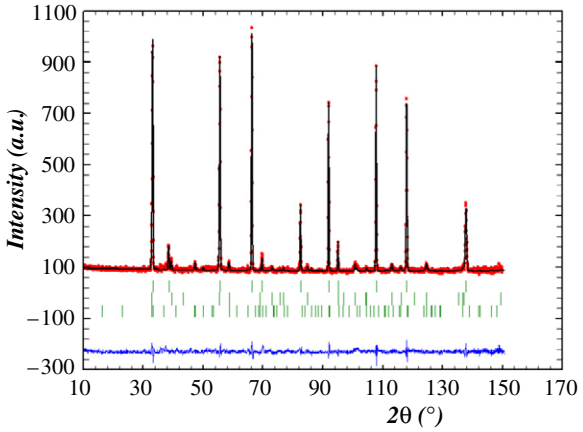

Figure 5. The neutron powder diffraction pattern of CoVSb in the paramagnetic phase at 100 K. The plotted points show the observed counts and the full curve is the calculated profile. The inset at the bottom is the difference between the observed and calculated patterns. The calculated positions of the reflections for the three phases, CoVSb, CoSb and Sb_4V, are shown as vertical lines.

the goodness of the fits obtained in the profile refinements; it is defined by

$$\chi^2 = \frac{\sum_{\text{obs}}[(I_o - I_c)/\sigma I_o]^2}{N_o - N_p}$$

where I_o and I_p are the observed and calculated intensities for the N_o measured points, σI_o is the estimated standard deviation of I_o and N_p is the number of fitted parameters.

3. Results

The neutron powder diffraction pattern of CoVSb obtained in the paramagnetic phase at 100 K is shown in figure 5. Eleven strong reflections occur in the angular range $5° < 2\theta < 157°$ which could be indexed on an fcc lattice with a lattice parameter of 5.7914 Å. A series of preliminary refinements were carried out assuming a $C1_b$ structure with space group $F\bar{4}3m$

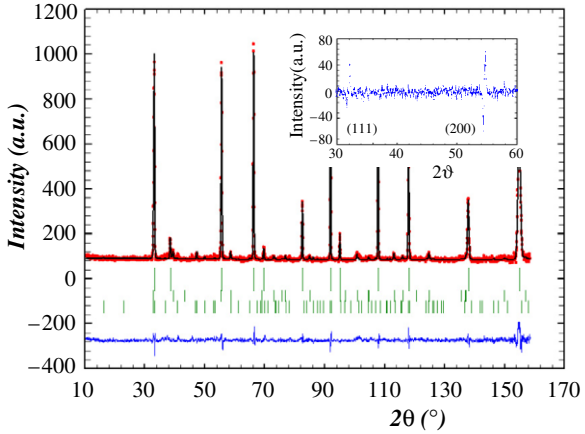

Figure 6. The neutron powder diffraction pattern of CoVSb in the ferromagnetic phase at 2 K. The plotted points show the observed counts and the full curve is the calculated profile. The inset at the bottom is the difference between the observed and calculated patterns. The calculated positions of the reflections for the three phases, CoVSb, CoSb and Sb_4V, are shown as vertical lines. The inset on the top left shows the difference pattern (2 K pattern −100 K) of the (111) and (200) Bragg reflections.

Table 3. Crystal and magnetic structure of the $C1_b$ phase of CoVSb.

Cubic $C1_b$ structure, space group $F\bar{4}3m$			
Sb 4a 000	Co 4b $\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$	V 4c $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$	Void 4d $\frac{3}{4}\ \frac{3}{4}\ \frac{3}{4}$
	2 K		100 K
a (Å)	5.7903(2)		5.7914(2)
	Ferromagnetic		Paramagnetic
Co moment (μ_B)	0.12(3)		—
V moment (μ_B)	0.11(2)		—
Sb occupancy	1		1
Co occupancy	1		1
V occupancy	1		1
χ^2	1.80		1.77

in which the (4b) site was systematically occupied by the three constituent elements. This analysis showed that the phase indeed had the $C1_b$ structure with the cobalt atoms occupying the 4b site (figure 1). In addition to the 11 distinct peaks the diffraction pattern contained a number of much weaker reflections which could be accounted for by assuming the presence of two impurity phases. One phase was identified as being CoSb, which has a hexagonal structure with lattice parameters $a = 3.9$ Å and $c = 5.179$ Å. CoSb, which has the space group $P6_3/mmc$ with Co located at (2a) (000) and Sb at site (2c) (0.333, 0.667, 0.25), is reported to be a weak paramagnet [16]. The other impurity phase was identified as having the Sb_4V_5 tetragonal structure with lattice parameters of $c = 9.581$ Å and $a = 3.559$ Å. The space group of Sb_4V_5 is $I4/m$ with the Sb atoms occupying (000) and (0.061, 0.286, 0) and the vanadium atoms located at (0.319, 0.393, 0). A further refinement was carried out based on a model containing the $C1_b$ structure, the hexagonal CoSb and tetragonal Sb_4V_5 phases. This model accounted for all of the observed reflections and did not generate any additional ones. The results of the refinement, for which $\chi^2 = 1.77$, are given in table 3. In the refinement the

site occupancies were allowed to vary but no significant deviation from the ideal $C1_b$ structure with the cobalt atoms occupying the (4b) sites was observed. The relative amounts of the $C1_b$ and impurity phases were determined as ~97% and 2% (CoSb) and 1% (Sb_4V_5) respectively.

Apart from a small contraction in the lattice parameters there was no significant change in the Bragg reflections on cooling to 50 K and then to 2 K as shown in figure 6.

At 2 K the compound is in the ferromagnetic state but the absence of substantial change in the diffraction pattern suggested that the magnetic scattering was small and commensurate with the nuclear lattice. In line with the assumptions used in the band structure calculations a refinement was carried out in which both the cobalt and vanadium atoms were allowed to carry a moment. The moments obtained in this refinement, which had a $\chi^2 = 1.8$, are given in table 3. It may be seen that the refinement leads to small moments on both atoms with a combined value per formula unit close to that obtained from magnetization measurements. However, fixing the moment at 0.17 μ_B and allowing it to reside either on the V or Co atoms only led to a slightly poorer fit. Although the magnetic scattering is small, significantly worse agreement was obtained by allowing the cobalt and vanadium moments to take the values calculated for the CoVSb structure as given in table 1. However, the 200 reflection, which has a small nuclear structure factor, is particularly sensitive to the size of the moment in the unit cell. Its intensity is predicted to increase by 60–100% for the three CoVSb models given in table 1. In figure 7(a) the refined magnetic and nuclear intensity of the 200 reflection is compared with that measured. As can be seen the agreement is good. A substantial difference is obtained, as shown in figure 7(b), if the vanadium and cobalt atoms are allowed to have moments of 1.19 and −0.19 μ_B as given in table 1.

4. Discussion

The bulk magnetic properties reported here are in close agreement with those determined by Terada *et al* [17]. However, both the magnetic [18] and electrical [19] properties are reported to depend on atomic order. Kaczmarska [18] and Terada [17] annealed their samples at a temperature of 750 °C. This temperature is lower than that used in the present experiment and therefore the atomic disorder may be expected to be less. However, the neutron measurements show that a sample quenched from 850 °C is highly ordered in the $C1_b$ CoVSb structure. Furthermore, they also show that the magnitude of the atomic moments is small in agreement with the bulk magnetization. Whether the moment ~0.17 μ_B is located on the vanadium or cobalt atoms could not be distinguished. However, similar measurements on related Co_2VZ compounds with the Heusler structure [20] would suggest that the moment is principally associated with the cobalt atoms. The size of the ground state moment and Curie temperature are similar to values observed in other weak itinerant ferromagnets [21]. The paramagnetic moment obtained from the Curie–Weiss susceptibility in CoVSb is approximately eight times larger than the ordered ground state value which again is consistent with weak itinerant ferromagnetism.

The magnetic and structural properties of related Heusler alloys X_2YZ in which the magnetic moment is confined to the Y atoms depend on the electron concentration. In these systems the Y atoms are separated by $a/\sqrt{2}$ typically 4.2 Å and consequently there is negligible d overlap and so the materials have localized magnetic properties. In the $C1_b$ structure XYZ, the atoms of the same type are also separated by $a/\sqrt{2}$ and it has been suggested that the electron concentration is again important in characterizing the physical properties. In a simple model based on the filling of orbitals the gap essential for half-metallic behaviour arises due to the hybridization of low energy cobalt d states with vanadium d states of higher energies forming bonding and anti-bonding bands. Since antimony can accommodate eight electrons

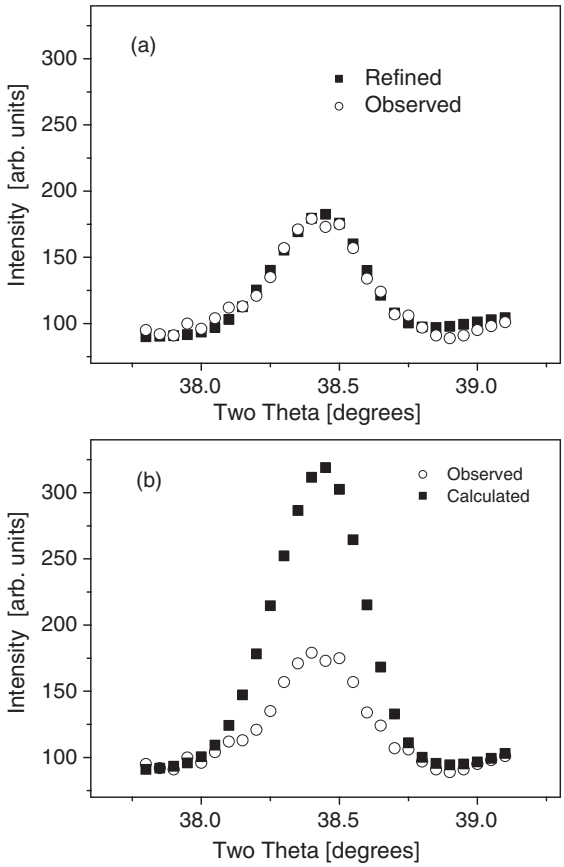

Figure 7. (a) The observed and calculated profiles of the (200) reflection from CoVSb at 2 K using the refined parameters given in table 3. (b) The observed and calculated profiles of the (200) reflection from CoVSb at 2 K. The calculated profile comprised the refined nuclear component and a magnetic part determined using a vanadium moment of 1.19 μ_B and cobalt moment of -0.19 μ_B as determined by band structure calculations [9].

in its sp bands, compounds with 18 valence electrons are predicted to be particularly stable, having a full bonding band with semiconducting properties and zero spin. Increasing the number of valence electrons beyond 18 requires the additional electrons to be accommodated in states above the gap. Since CoVSb has 19 valence electrons, the extra electron has to be located in an anti-bonding state, which leads to a moment of 1 μ_B per formula unit. This conclusion is supported by band structure calculations, which predict a vanadium moment slightly in excess of 1 μ_B in CoVSb with ($C1_b$) atomic order as shown in table 1. The criteria for the formation of a local moment in metallic vanadium have been discussed by Hattox *et al* [22]. In CoVSb the V–V separation is 4.1 Å, which on the basis of the calculations by Hattox *et al* would lead to a vanadium moment of $\sim$0.8 μ_B in line with the band structure calculations for CoVSb. However, the magnetic moment determined experimentally is significantly smaller than the values predicted by band structure calculations. It has been suggested that this may arise due to the rapidly varying density of states close to the Fermi energy [10]. Calculations show that a small variation in the exchange parameter changes the ground state from para- to ferromagnetic. However, polarized neutron diffraction measurements on cobalt based Heusler

alloys show that the moment on the cobalt atoms is of predominantly e_g character and that the minority spin band is also occupied. The occupancy of the minority band was found to increase in those compounds in which manganese had been replaced by other non-magnetic transition metals. This is consistent with the experimental results showing CoVSb to be a weak itinerant ferromagnet. Based on the polarized neutron measurements it is possible that the moment observed in CoVSb has a significant orbital contribution. Polarized neutron measurements would enable this conjecture to be elucidated.

5. Conclusion

The atomic order in CoVSb has been established by neutron powder diffraction and together with magnetization measurements it has been shown that the compound is a weak itinerant ferromagnet. It is clear that CoVSb does not have the predicted half-metallic properties required for spin injection in new electronic devices. This finding is in line with other neutron diffraction measurements on Co_2MnSi [23] and Co_2S [24] that have also failed to confirm the predicted half-metallic ferromagnetic properties.

References

[1] Kautzky M C, Mancoff F B, Bobo J-F, Johnson P R, White R L and Clemens B M 1997 *J. Appl. Phys.* **81** 4026
[2] Moodera J S, Kinder L R, Wong T M and Merservey R 1995 *Phys. Rev. Lett.* **74** 3273
[3] Kämmerer S, Heitmann S, Meyners D, Sudfield D, Thomes A, Hütten A and Reiss G 2003 *J. Appl. Phys.* **93** 7945
[4] Prinz G A 1999 *J. Magn. Magn. Mater.* **200** 57
[5] Ishida S, Akazawa S, Kubo Y and Ishida J 1982 *J. Phys. F: Met. Phys.* **12** 1111
[6] de Groot R A, Mueller F M, van Engen P G and Buschow K H J 1983 *Phys. Rev. Lett.* **50** 2024
[7] Hobbs D and Hafner J 1999 *J. Phys.: Condens. Matter* **11** 8197
[8] Lewis S P, Allen P B and Saski T 1997 *Phys. Rev.* B **55** 10253
[9] Ishida S, Masaki T, Fujii S and Asano S 1997 *Physica* B **239** 163
[10] Tobola J, Pierre J, Kaprzyk S, Skolozdra R V and Kouacou M A 1998 *J. Phys.: Condens. Matter* **10** 1013
[11] Galanakis I, Dederichs P H and Papanikolaou N 2002 *Phys. Rev.* B **66** 134428
[12] Nanda B R K and Dasgupta I 2003 *J. Phys.: Condens. Matter* **15** 7307
[13] Evers C B H, Ricter C G, Hartjes K and Jeitschko W 1997 *J. Alloys Compounds* **252** 93
[14] Kittel C 1996 *Introduction to Solid State Physics* (New York: Wiley)
[15] Rodriguez-Carvajal J 1997 *FullProf version 3.3* Laboratoire Leon Brillouin
[16] Chen T, Rogowski D and White R M 1978 *J. Appl. Phys.* **49** 1425
[17] Terada M, Kendo K, Fujita Y and Kimura R 1972 *J. Phys. Soc. Japan* **32** 91
[18] Kaczmarska K, Pierre J, Beille L, Tobola J, Skolozdra R V and Melnik G A 1998 *J. Magn. Magn. Mater.* **187** 210
[19] Nobota T, Ito M, Kurisu M and Makihara Y 1995 *Abstract of the Meeting of the Physical Society of Japan Sectional Meeting* part 3, p 100
[20] Ziebeck K R A and Webster P J 1974 *J. Phys. Chem. Solids* **35** 1
[21] Moriya T (ed) 1985 *Spin Fluctuations in Itinerant Electron Magnetism* (Berlin: Springer)
[22] Hattox T M, Conklin J B, Slater J C and Trickey S B 1973 *J. Phys. Chem. Solids* **34** 1627
[23] Brown P J, Neumann K-U, Webster P J and Ziebeck K R A 2000 *J. Phys.: Condens. Matter* **12** 1827
[24] Brown P J, Neumann K-U, Simon A and Ziebeck K R A 2005 *J. Phys.: Condens. Matter* **17** 1583