Journal of Alloys and Compounds 577 (2013) 417–425

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Effect of site disorder on the electronic properties of Fe_2VAl Heusler alloy

Ch. Venkatesh [a,*], V. Srinivas [a,c], V.V. Rao [b], S.K. Srivastava [a], P. Sudheer Babu [d]

[a] Department of Physics and Meteorology, Indian Institute of Technology, Kharagpur, India
[b] Cryogenic Engineering Centre, Indian Institute of Technology, Kharagpur, India
[c] Department of Physics, IIT Madras, Chennai, India
[d] Department of Physics, RGUKT, Nuzvid, Andhra Pradesh, India

ARTICLE INFO

Article history:
Received 8 April 2013
Received in revised form 22 May 2013
Accepted 24 May 2013
Available online 4 June 2013

Keywords:
Heusler alloys
Impurity and defect levels
Magnetoresistance
Density functional theory
Magnetic impurity interactions

ABSTRACT

Ab initio calculations on ordered $L2_1$ structure of Fe_2VAl alloy have been carried out by introducing B2, DO_3, A2′ and XY–XZ type disorders in order to understand the role of anti-site disorder on magnetic and transport properties. These studies show an enhancement of individual spin moments of anti-site Fe atoms in DO_3, A2′ and XY–XZ type anti-site disorder, making the Fe_2VAl alloy magnetically active. These calculations also show that hybridization due to covalent distribution of valance states among the atoms is important in Fe_2VAl, defining its unusual physical properties. From the density of states spectrum obtained near the Fermi level, we have noticed formation of intermediate defect-like states that couple the edges of the pseudo gap on both sides of the Fermi level, driving the material from semi-metallic to metallic type in electrical transport. We also present experimental results on structural, magnetic and electrical properties of Fe_2VAl Heusler alloy. A comparison of present experimental data with calculations shows an existence of DO_3 type anti-site disorder due to the Al-deficiency in Fe_2VAl alloy which causes deviations in theoretical results on the magnetic and transport behaviour of pure Fe_2VAl. The temperature dependence of electrical transport and magnetic data analysed on the basis of impurity band model which provides convincing evidence for itinerant character of this alloy system with an anti-site disorder.

1. Introduction

Among Fe-based Heusler alloys, Fe_2VAl Heusler alloy has attracted the attention of scientific community from both fundamental physics as well as industrial application point of view [1]. Several inconsistencies are noticed in experimental investigations on electrical transport and magnetic properties of this alloy. Some experiments show a steep rise in the electrical resistivity (ρ) in the low temperature region, reminiscent of a semiconductor [2–5] with a finite band gap, while others have reported a metallic behaviour [6,7] below a transition temperature (T_P) where ρ goes through a maximum. These discrepancies are attributed to the presence of anti-site defects due to variations in sample preparation and processing conditions [2–7]. Nishino et al. [4] reported that the magnetic anti-site defects arise mainly due to Fe–V stoichiometric variations during heat treatment of the alloy. This was further supported through specific heat measurements on Fe_2VAl [8] where an enhancement in effective mass of the carriers due to spin fluctuated scattering with anti-site defects has been reported. Alternatively, the raise of specific heat at low temperature was attributed to spin fluctuations [8,9] or excitonic correlations [10]. On the other hand, Naka et al. [11] suggested an existence of Quantum Critical Phase (QCP) in $Fe_{2+x}V_{1-x}Al$ ($x = 0.05$) alloy at lower temperatures that leads to the enhancement in specific heat. Singh et al. [12] predicted that an anti-site induced local magnetic moment drives the Fe_2VAl alloy into a spin glass state and experiments also show magnetic glass behaviour [2,5]. From the Mössbauer measurements on $Fe_{2.4}V_{0.6}Al$ alloy, Popiel et al. [13] showed that the magnetic properties depend entirely on crystal structure. They demonstrated that the A2-type disordered structure exhibits ferromagnetic properties, while B2 and DO_3-type structures do not. Recently, Saha et al. [14] observed that substitution of Cr in $L2_1$ structured Fe_2VAl results in development of B2 type structure and enhancement in magnetic character. All these observed changes could be attributed to development of anti-site disorder in the ordered Fe_2VAl lattice. The recent band structure calculations [15,16] suggest that an inclusion of anti-site disorder modifies the thermoelectric power factor (P) values of the ordered semiconductor-like Fe_2VAl. These observations suggest that the experimentally obtained DOS [17,18] at Fermi level do not agree with the theoretically predicted DOS spectrum due to inherent structural disorder/defects.

Although, several qualitative explanations were proposed in the literature to elucidate the disorder induced magnetic behaviour of Fe_2VAl alloy, the effect of disorder on the physical properties of

* Corresponding author. Tel.: +91 3222283848.
E-mail address: venkyphysicsiitm@gmail.com (Ch. Venkatesh).

0925-8388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2013.05.175

well ordered Fe_2VAl alloy is still not clear. Therefore, we believe that studies on variation of band structure near the Fermi level while introducing systematic disorder in perfectly ordered $L2_1$ lattice would be interesting. Such studies not only provide an in-depth understanding of unusual electronic properties of this material but also help in development of new materials with controlled disorder for industrial applications. Hence, an attempt has been made here, to investigate the effect of structural disorder on the transport and magnetic properties of Fe_2VAl using Density Functional Theory (DFT) calculations. A comparison is also made with different types of anti-site disorders in order to gain a better insight into the physical properties of Fe_2VAl alloy. Further, structural, magnetic and electrical properties have been investigated for the anti-site disordered sample and compared with the theoretical calculations. These results along with the literature data could provide a better insight into the effect of anti-site disorder on physical properties of Fe_2VAl alloy. The resulting magnetic character could be explained by the cluster-like behaviour of impurity spins and the obtained magnetotransport behaviour is explained on the basis of impurity states model originally proposed for dilute magnetic alloys by Korringa et al. [19].

2. Experimental details

Fe_2VAl alloy was prepared by arc melting high purity elemental constituents and subsequent heat treatment was carried out in vacuum at 1273 K for two days. The ingot was then quenched in liquid nitrogen and annealed to at 873 K to relax the quenched disorder. The ingot was cut into suitable shapes (2 mm × 2 mm × 8 mm) using spark-erosion technique for physical property measurements. The crystallographic structure was identified using Powder X-ray Diffraction (XRD) pattern taken with Cu Kα radiation of wavelength $\lambda = 0.15418$ nm using a P.W. 1718 X-ray diffractometer. The magneto transport measurements were carried out using cryogen free superconducting magnet (Model: 5TL-VRTB30, Janis Research Company, USA) in the temperature range 7–300 K under external magnetic fields up to 4.6 T. The magnetization measurements were carried out from 2 K to 300 K using Ever Cooled SQUID VSM (Quantum Design, USA). For the ageing experiments, sample was cooled in zero fields from room temperature until the temperature of the measurement, T_m, is reached. After waiting time, t_w (100 S), a small probe field, H (100 Oe), is applied and magnetization is recorded as a function of time.

3. Results and analysis

3.1. Crystal structure

The unit cell of Heusler-type intermetallic compounds with a stoichiometric formula X_2YZ, comprises four inter-penetrating fcc sublattices with the atoms located at A(000), B(1/4 1/4 1/4), C(1/2 1/2 1/2), and D(3/4 3/4 3/4) of $L2_1$ lattice. There are several ways in which the atoms X, Y and Z can be distributed over these lattice sites A, B, C and D which generates various types of preferential anti-site disorder [20] as given in Table 1. The XRD pattern was analysed with a Rietveld structural analysis using FULLPROF 2 K (version 3.4) [21] program and plotted along with the residues as shown in Fig. 1a. The analysis of XRD data suggests a cubic structure with Fm3m space group and the presence of (1 1 1) superlattice peak with very weak intensity (inset in Fig. 1a) indicating the $L2_1$ type ordering in the sample. In addition, each peak exhibits a shoulder at lower angle side which is fitted with the anti-site DO_3 phase Fe_3Al along with the $L2_1$ Fe_2VAl. The composition analysis carried out using EDAX investigation (Fig. 1b) during the topography scan at different regions of the sample confirms the deficiency of Al content. Recently, Sato et al. [22] have also reported that the deficiency in Al-content encourages the substitution of Fe/V-atoms into Al-site for $Fe_2VAl_{0.95}$ alloy and hence, the possibility of presence of DO_3 disorder is not ignored here. The volume of the DO_3 phase was obtained to be 14.5% which may be the origin of unusual physical properties in Fe_2VAl alloy. Further, the experimental data combined with DOS calculations also show the presence of a significant amount of DO_3 disorder in Fe_2VAl alloy.

3.2. Ab-initio calculations

In order to address the observed variations in electronic properties of Fe_2VAl alloy [2–7], it is important to study the band structure variations around the Fermi level inhibited by the presence of various types of anti-site disorder. Since it is difficult to produce a material with precise control on the site-disorder experimentally, one can investigate such an effect through simulation study by retaining the basic structure and nominal composition. The ab initio DOS calculations were performed on ordered and disordered structures of Fe_2VAl composition using WIEN2k package [23] by considering the Linear Augmented Plane Wave (LAPW) theory [24] with Generalized Gradient Approximation (GGA) [25,26] for exchange and correlation of electrons. We have used −95.242 eV as an energy cut-off for the plane wave expansion and the radius of muffin-tin (RMT) for all the atoms were taken to be 2.2 Å. The value of RMT was reduced by 2% for self consistent field (scf) calculation which is further reduced to 4–6% for volume optimization. The number of K-points was taken to be 32 for irreducible Brillouin Zone (BZ) and $\Delta q = 0.0001$ coulombs has been used as a condition for scf convergence. The value of $R_{MT}K_{MAX}$ was kept at 7, where R_{MT} is the smallest value among all atomic radii and K_{MAX} is the cut-off wave number for the plane waves. The calculations were done on a $L2_1$ primitive type lattice structure of Fe_2VAl.

A schematic diagram of the first nearest neighbour (NN) of Fe-atoms (see Table 1) is depicted in Fig. 2a for ordered as well as disordered structures using which DOS calculations have been performed and discussed below. In Fig. 2b–f, partial DOS for ordered as well as disordered structures are shown. Here, the contribution of Al-p states to the DOS spectrum is very small and hence neglected. On close observation of Fig. 2b, one can notice the formation of pseudogap near the Fermi level in the DOS spectrum, which is responsible for semi-metallic nature of this intermetallic alloy. Further, there is a symmetric distribution of anti-bonding states of both spin up and spin down bands, suggesting paramagnetic ground state for an ordered Fe_2VAl according to the Slater's band theory of magnetism [27]. Indeed, existence of pseudo-gap near the Fermi level was theoretically suggested earlier [10,12,28] for both spin sub-bands of $L2_1$–Fe_2VAl. The pseudogap in the $L2_1$–Fe_2VAl has been ascribed mainly to the strong d–d and p–d hybridization effects. As suggested in earlier reports [29,30], an interaction between the orbitals of Fe–Fe (second NNs) takes place preferably

Table 1
A brief summary of the anti-site disorders derived by the inclusion of 25 % disorder in the ordered $L2_1$ structure used for DOS calculations and their respective P values.

Anti-site disorder type	Displaced atoms	NN arrangement around the Fe-site	$P = S^2$ (arb. units)
$L2_1$ (ordered)	–	4V, 4Al	0.0326
B2	1V↔1Al	4V, 4Al	4398
DO_3	1Fe↔1V	7Fe, 1V	1593
A2′	1Fe↔1Al	7Fe, 1A1	1579
XY–XZ	1Fe↔1V	6Fe, 1V, 1Al	125
(DO_3 + A2′)	1Fe↔1Al		