Journal of Solid State Chemistry 216 (2014) 56–64

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Toward a better understanding of the magnetocaloric effect: An experimental and theoretical study of $MnFe_4Si_3$

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ARTICLE INFO

Article history:
Received 13 February 2014
Received in revised form
29 April 2014
Accepted 5 May 2014
Available online 10 May 2014

Keywords:
Magnetocaloric effect materials
Intermetallic
Silicide
Magnetism
Neutron diffraction
Density functional theory

ABSTRACT

The intermetallic compound $MnFe_4Si_3$ has been studied by high-resolution Time of Flight (TOF) neutron powder diffraction. $MnFe_4Si_3$ crystallizes in the hexagonal space group $P6_3/mcm$ with lattice constants of $a=b=6.8043(4)$ Å and $c=4.7254(2)$ Å at 310 K. Magnetic susceptibility measurements show clearly the magnetic transition from paramagnetism to ferromagnetism at about 302(2) K. Magnetic structure refinements based on neutron powder diffraction data with and without external magnetic field reveal strong evidence on the origin of the large magnetocaloric effect (MCE) in this material as a partial reordering of the spins between ~270 K and 300 K. In addition, electronic structure calculations using the self-consistent, spin-polarized Tight Binding-Linear MuffinTin Orbital (TB-LMTO) method were also accomplished to address the "coloring problem" (Mn/Fe site preference) as well as the unique ferromagnetic behavior of this intermetallic compound.

1. Introduction

In the past decade, a rapid development of a new magnetic refrigeration technology, based on the magnetocaloric effect (MCE), has attracted increasing interest in magnetic materials. Magnetic refrigeration, which is based on the entropy changes of magnetic materials in an applied magnetic field, exhibits more considerable advantages than conventional vapor-cycle refrigeration, such as high energy efficiency, small volume, ecological cleanliness, etc. Until recently, the best candidates known were gadolinium (Gd) based materials such as $Gd_5Ge_2Si_2$ [1–5] or arsenides such as $MnFeP_{1-x}As_x$. [6–9] However, the high cost of Gd and the toxicity of As make it questionable whether current materials based on either technology could be deployed commercially. Therefore, materials research in the magnetic cooling field has been mainly focused on the search for new low cost/environment friendly materials displaying satisfactory MCEs.

As part of an effort to gain a better understanding of the chemical and physical parameters which drive the MCE and to potentially design new magnetic materials, we reinvestigated the magnetic and the crystallographic structure of $MnFe_4Si_3$. Our interest of studying that specific Mn/Fe composition was driven by a recent work reported by Songlin et al.[10] showing a unique MCE effect for that specific Mn/Fe composition along the $Mn_{1-x}Fe_xSi_3$ series. They reported the magnetic susceptibility of $MnFe_4Si_3$ shows clearly that this phase undergoes a sharp paramagnetic–ferromagnetic transition at 302(2) K associated with a MCE of up to 3 J/kg K^{-1}, by applying an external magnetic field of only 3 T (see Fig. 1). Our studies were performed at various temperatures and magnetic fields in order to understand the response of such external contributions to the magnetic and the crystallographic structures. Our magnetic structure refinements based on neutron powder diffraction data under magnetic field near room temperature strongly suggest that the origin of the MCE properties in this class of material is a partial reordering of the spins. Furthermore, electronic structure calculations using the self-consistent, spin-polarized TB-LMTO method were also performed to understand the unique physical properties of the $MnFe_4Si_3$ intermetallic compound, especially the "coloring problem" (Mn/Fe site preference), the low temperature ferromagnetism, and also its almost half-metallic behavior.

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http://dx.doi.org/10.1016/j.jssc.2014.05.001
0022-4596/Published by Elsevier Inc.

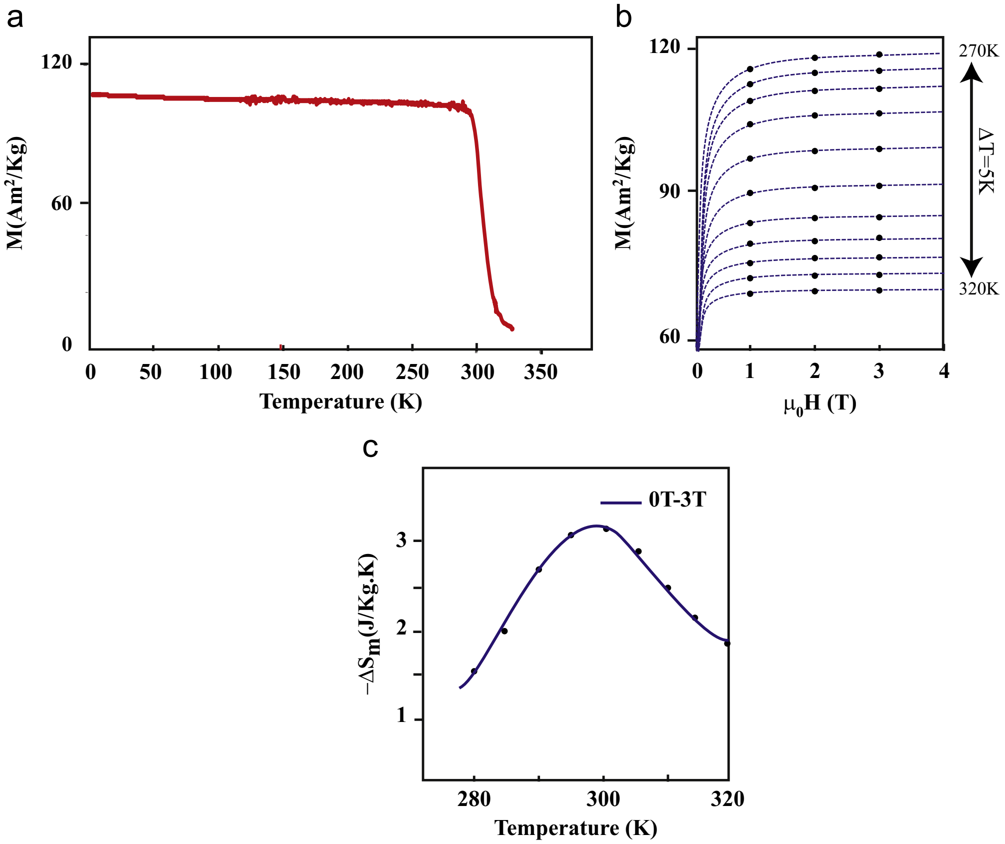

Fig. 1. Temperature dependence of the (a) dc magnetization, (b) field dependence of the magnetization at various temperatures from 270 K to 320 K (black dots) and (c) entropy change, between 0 T and 3 T, calculated based on the magnetization measurements using Eq. (2). Blue lines in (b) and (c) are guides for the eyes. See the text for further details. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Experimental section

$MnFe_4Si_3$ polycrystalline samples have been prepared by melting with induced current method under Argon. For further information on the preparation technique see Ref. [11] and references within. Every batch was melted and annealed at least four times to ensure homogeneity. Mn (Aldrich, 99.99%), Fe (Aldrich, 99.99%) and Si (Aldrich, 99.99%) were used as starting materials. The Mn metal pieces were preliminary melted under argon so that oxidation could be easily removed from the surface. All final products remain with a metallic luster and are visibly stable upon exposure to both air and moisture over several weeks.

The phase purities of the products were analyzed using energy dispersive spectroscopy (EDS) by a JEOL 840A scanning electron microscope, equipped with an IXRF system Iridium X-ray analyzer with a Kevex Quantum thin-window Si(Li) detector for quantitative chemical analysis with Si as the internal standard. Data have been collected on various different points giving a homogeneous composition of the samples of $Mn_{0.97(3)}Fe_{4.1(2)}Si_3$ consistent with the composition expected. No significant oxygen contamination was observed during the data collection.

The dc magnetization as a function of temperature from 1.8 to 320 K and the magnetic field (from 0 to 4 T) were measured on a Quantum design (QD) Magnetic Property Measurement System (MPMS). Temperature-dependent magnetization data were collected after the $MnFe_4Si_3$ polycrystalline sample was placed in a gel-capsule fixed in a straw by measuring the field-cooled (FC) magnetization.

Due to the nearly indistinguishable X-ray scattering factor between Mn and Fe (one electron apart), neutron powder diffraction experiments were performed on a ca. 4 g powder sample of $MnFe_4Si_3$ to achieve better resolution of the transition metal site occupancies. Indeed, the elastic neutron cross sections for Mn (1.75 barn) and Fe (11.22 barn) are significantly different, which allows us to refine site distributions accurately. Moreover, as magnetic behavior is expected for $MnFe_4Si_3$, neutron scattering could give unique information on the magnetic ordering. Therefore, TOF neutron powder diffraction data were collected at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory on the new powder diffractometer Powgen. Differing from nearly all other time-of-flight (TOF) neutron powder diffractometers, the design of Powgen is based on combining the diffracted neutrons collected at all angles into a single profile rather than assigning them to series of different profiles that traditionally were based on grouping detectors according to scattering angle. Such a unique approach yields to a high count rate while preserving good resolution $\Delta d/d = 0.0015$ at $d = 1$ Å. Further information on the design of Powgen could be found in Ref. [12] and references therein. Data were collected at 310 K, 300 K, 270 K, 250 K, 220 K, 190 K, 160 K, 130 K, 100 K, 80 K, 50 K, 30 K and 10 K in that specific order. For each temperature data collections have been performed using a unique center wavelength (CWLs) of 1.066 Å, which covers a d-spacing range from 0.29 Å to 3.30 Å. This energy bandwidth has been ideally chosen in order to have accurate information on the nuclear/magnetic structure as well as on the atomic displacement parameters (ADPs).

Additional neutron powder diffraction data were also collected under 0 T and 3 T magnetic fields on the same sample in the vicinity of room temperature on the high-resolution neutron powder diffractometer HB2A at the High Flux Isotope Reactor at Oak Ridge National Laboratory, using 12′-31′-6′ collimation and a wavelength of 2.41 Å {Ge (113)}. Based on the expected