Journal of Magnetism and Magnetic Materials 410 (2016) 105–108

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Direct measurement of the magnetocaloric effect in cementite

B. Kaeswurm [a,*], K. Friemert [a], M. Gürsoy [b], K.P. Skokov [a], O. Gutfleisch [a,*]

[a] Geo- und Materialwissenschaften, Technische Universität Darmstadt, Darmstadt, Germany
[b] Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, Darmstadt, Germany

ARTICLE INFO

Article history:
Received 28 September 2015
Received in revised form
5 February 2016
Accepted 25 February 2016
Available online 27 February 2016

Keywords:
Magnetocaloric effect
Second order phase transition
Ferromagnetism
Cementite
Cohenite

ABSTRACT

Measurements of the magnetocaloric effect of cementite at its Curie temperature of 475 K are presented. An adiabatic temperature change of 1.76 ± 0.01 K was measured using a direct measurement technique. The isothermal entropy change was determined from measurements of magnetisation isotherms and was shown to be $3.07\ \mathrm{J\,K^{-1}\,kg^{-1}}$ in a field change of 2 T. The field dependencies of both magnetocaloric properties follow the $H^{2/3}$ dependence typical for ferromagnetic materials with a second order phase transition. The material may be of interest in magnetocaloric applications such as magnetic refrigeration or thermomagnetic power generation.

1. Introduction

The magnetocaloric effect (MCE) constitutes a change in thermodynamic properties at a magnetic transition temperature such as the Curie temperature, T_C [1–6]. Conventionally, samples heat up when a magnetic field is applied. Aside from being interesting from a fundamental scientific point of view, the effect finds application for cooling in low temperature physics by using paramagnetic salts to cool to very low temperatures [7]. The MCE is also considered for room temperature refrigeration technology using materials with a transition near room temperature [3,5] or for heat-to-power conversion [8,9], where an appropriate thermodynamic cycle is chosen to use the magnetocaloric material for power generation.

The magnetocaloric effect may be expressed in terms of entropy change, ΔS, under isothermal conditions or temperature change under adiabatic conditions, ΔT_{ad}. The entropy change quantifies how much heat can be moved by magnetic means while the adiabatic temperature change determines the temperature difference that can be achieved to transfer heat to and from the heat transfer fluid [5,10]. These quantities are related by Eq. (1) where C_p is the specific heat capacity.

$$dT_{ad}(\mu_0 H) = \frac{T}{c_p} dS(\mu_0 H) \tag{1}$$

The benchmark material in magnetic refrigeration is considered to be the rare earth element Gadolinium. When subjected to a magnetic field change from 0 T to 2 T (0 to 20 kOe) at its T_C of 294 K Gd shows $\Delta S = -10.4\ \mathrm{J\,kg^{-1}\,K^{-1}}$ and $\Delta T_{ad} = 5.8$ K [11]. Other well studied magnetocaloric materials include $Gd_5Ge_2Si_2$ [1], La(Fe,Si)$_{13}$ [12,13] and Fe_2P-based materials [14]. In order to be considered for application, the magnetocaloric material should be sustainable and environmentally-friendly. There is therefore a motivation to find novel rare earth free magnetocaloric materials [4,5,15]. The candidate material should possess a tuneable T_C, to be tuned to the temperature of application, which in the case of magnetic refrigeration is room temperature or above room temperature for power generation.

Fe_3C, known as cementite, cohenite or iron-carbide consists of widely available elements and as a binary system is comparatively simple to be studied both experimentally and theoretically. This compound has an orthorhombic crystal structure (space group *Pnma*, no. 62) [16] and a Curie temperature of $T_C \sim 475$ K which can be adjusted by substitution of various elements. For example substitution of 2.4 wt% Molybdenum has been shown to reduce T_C to 420 K [17]. The material is well studied including the mechanical and electrical properties [18–21]. Cementite plays a crucial role in the mechanical properties of steel. Studies of the pressure dependent magnetic properties of cementite have shown that at a high pressure of 25 GPa the material undergoes a magnetic collapse associated with a structural transition [22]. For a field change of 5 T an entropy change of $\Delta S = 3.4\ \mathrm{J\,Kg^{-1}\,K^{-1}}$ at 305 K has been reported for $(Fe_{0.9}Mn_{0.1})_3C$ [23] and $3.5\ \mathrm{J\,Kg^{-1}\,K^{-1}}$ at 360 K for $Fe_{2.85}Cr_{0.05}C$ [24]. A larger magnetocaloric effect is expected in pure cementite. The heat capacity has been shown by Umemoto to

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[*] Corresponding authors.
E-mail addresses: Barbara.Kaeswurm@fau.de (B. Kaeswurm), gutfleisch@fm.tu-darmstadt.de (O. Gutfleisch).

http://dx.doi.org/10.1016/j.jmmm.2016.02.080
0304-8853/

decrease with the addition of Cr and Mn [25] which is detrimental to possible application in magnetic refrigeration. No direct measurement of the magnetocaloric effect of pure cementite has been reported prior to this work. Here we present an assessment of both magnetocaloric properties ΔS and ΔT_{ad} as well as a study of the field dependence of the same, confirming the $H^{2/3}$ dependence expected for a second order transition [26,27]. Knowledge of the field dependence is crucial as in present designs the most significant cost contribution in a magnetic refrigerator is the permanent magnet. In this work we present an investigation of the magnetocaloric properties of cementite and assessment of its potential use in application.

2. Experimental techniques

Powders of the constituting elements were mixed by high energy ball milling in a SPEX 8000D with a ball to powder ratio of 10:1 for 100 min. The sample was then compacted by field assisted sintering (SPS) for 30 min at a temperature of 1083 K and pressure of 100 MPa. A carbon mould was used and the shape of the final sample was a pellet of 1 cm diameter. The structure and composition of the sample was characterised by x-ray diffraction in Bragg–Bretano configuration with Cu $K_{\alpha 1,2}$ radiation. The density was determined by making use of the Archimedes principle in order to examine the porosity and determine the volumetric entropy change which is an important engineering parameter.

The magnetic properties were studied using a LakeShore Vibrating Sample Magnetometer with variable temperature setup. The temperature dependent magnetisation was measured in a low non-saturating field of 0.05 T (500 Oe) in order to evaluate T_C. Magnetisation isotherms $M(H)_T$ were measured in fields up to 2 T (20 kOe). From these the magnetic entropy ΔS was calculated using the Maxwell relation [28].

The adiabatic temperature change ΔT_{ad} was measured directly in a bespoke device where the magnetic field was provided by permanent magnets arranged in two Halbach cylinders. Rotation of the cylinders with respect to each other enabled magnetic fields from 0 T to 1.93 T (0 to 19.3 kOe). The evacuated sample space was situated in the common bore of the cylinders, the sample being thermally shielded from the environment with glass fibre. The temperature of the sample was measured as a function of the applied field and compared to the temperature of the sample holder. Accuracy better than 0.01 K was provided by a T-Type thermocouple (copper-constantan).

3. Results

The X-ray diffraction pattern of the sample obtained using Cu-radiation is shown in Fig. 1(b). The pattern shows that the sample exists in the expected structure (space group *Pnma*, no. 62) with lattice parameters $a = 5.089 \pm 0.001$, $b = 6.749 \pm 0.001$ and $c = 4.526 \pm 0.001$, which means the unit cell of the sample studied is slightly expanded compared to values reported elsewhere [16]. No traces of elemental Fe are observed within the sensitivity of the measurement. A density of 7.55 g cm^{-3} was obtained using an Archimedes balance. This is 98% of the full density of 7.68 g cm^{-3} [21]. The insert in Fig. 1(a) shows a backscattered electron image of the sample. Visible in black are pores and in lighter colour iron rich regions. Overall a phase purity of 96% with 2% pores and 2% Fe is estimated.

The temperature dependent magnetisation in a low non-saturating field of 0.05 T (500 Oe) can be seen in Fig. 2. The derivative of the curve is also displayed. A T_C of 475 K is observed in agreement with literature.

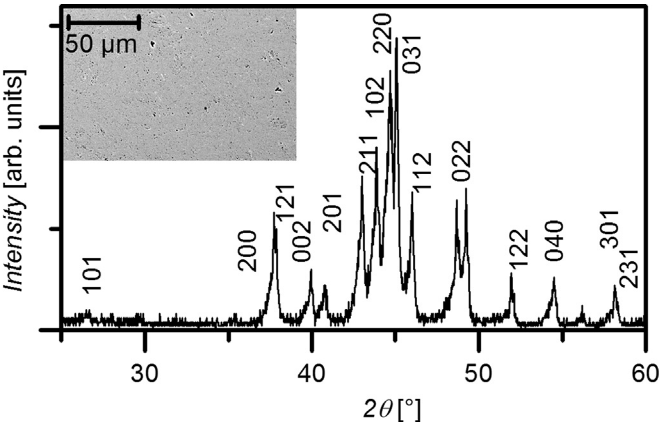

Fig. 1. X-ray Diffractogram using Cu radiation in a Bragg Bretano configuration. Inset: Backscattered Electron Micrograph of the cementite sample studied.

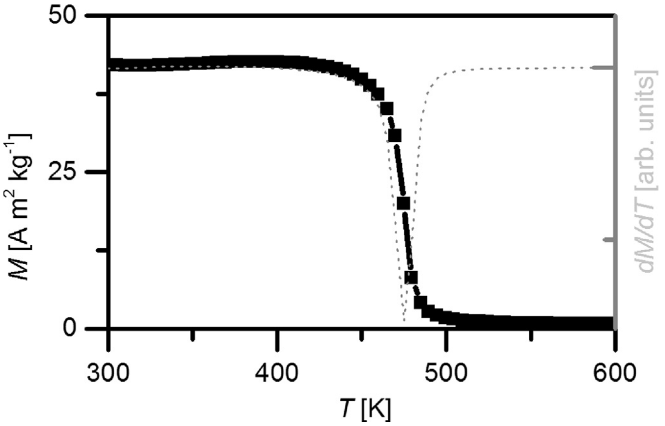

Fig. 2. Temperature dependent magnetisation (left hand axis) and its derivative (r. h.a.) in a field of 0.05 T (500 Oe). A Curie Temperature of T_C of 475 K is observed.

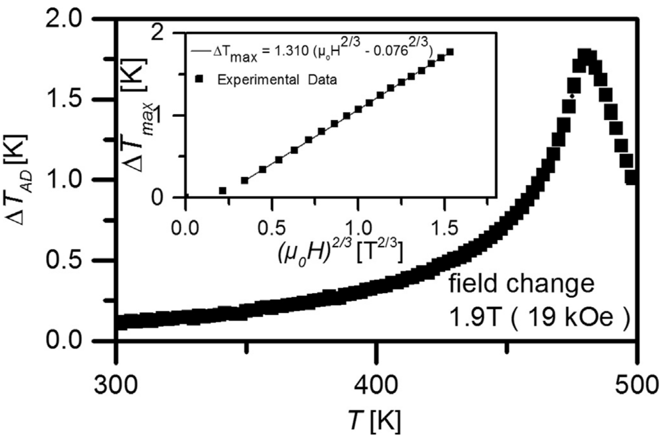

Fig. 3. Direct measurement of adiabatic temperature change in a field of 1.9 T (19 kOe). Inset: magnetic field dependence of the maximum adiabatic temperature change.

The direct measurement of ΔT_{ad} is shown in Fig. 3. At 480 K a ΔT_{ad} of 1.76 ± 0.01 K is measured, which is three times lower than that of Gd at room temperature. The inset of Fig. 3 shows the field dependence of the maximum ΔT_{ad}. In the range of 0.2 T to 2 T the maximum adiabatic temperature change follows a $H^{2/3}$ dependence as expected for second order phase transitions [26,27]. In this region the experimental data follows the equation $\Delta T_{max} = A(\mu_0 H^{2/3} - \mu_0 H_*^{2/3})$ for $A = 1.310$; $\mu_0^{2/3} T^{2/3}$and $H_* = 0.076T$.