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Abstract

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Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Debnath, J. C. & Wang, J. Li. (2016). Magnetocaloric effect in HoMn₂Si₂ compound with multiple magnetic phase transitions. *Intermetallics*, 78 50-54.

Magnetocaloric effect in HoMn_2Si_2 compound with multiple magnetic phase transitions

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Abstract:

The structural, magnetic and magnetocaloric properties of the polycrystalline compound HoMn_2Si_2 have been studied. The temperature variation of magnetization and heat capacity show that below room temperature the compound undergoes multiple magnetic transitions, at about 80, 15 and 3.5 K respectively. Moreover, the presence of the interesting thermomagnetic irreversibility in HoMn_2Si_2 is detected in the magnetization versus temperature plot, which can be ascribed to the narrow domain wall pinning effect. A broad and asymmetric peak is observed for the MCE response which might suggest the underlying first-order nature of the transition and/or the spin fluctuations of the Mn subsystem. The density of states $N(E_F)$ at the Fermi level and the Debye temperature have been determined and analyzed. Large magnetocaloric effect ($\Delta S_M = -9$ J/kg-K for a field change of 5 T around 9 K) suggest that this material is suitable for the low temperature magnetic refrigeration.

Keywords: Intermetallics; HoMn₂Si₂ compound; Magnetocaloric effect; Magnetic phase transition;

1. Introduction

In recent years, the magnetic refrigeration, a green cooling technology based on magnetocaloric effect (MCE), an intrinsic phenomenon of a magnetic material has attracted much attention due to its higher energy efficiency and eco-friendliness than the commonly used conventional gas compression refrigeration which uses a magnetic field to change the magnetic entropy of a material [1-6]. The MCE is an intrinsic phenomenon of magnetic materials, which manifests as an isothermal magnetic entropy change (ΔS_M) or an adiabatic temperature change (ΔT_{ad}) when the magnetic material is exposed to a varying magnetic field. Large values of ΔS_M and ΔT_{ad} under a varying magnetic field are considered to be the most important indicator of magnetic cooling materials for the practical application, and therefore it is important to find new materials with large MCE. So to search for magnetic materials with large values ΔS_M and ΔT_{ad} is the main mission in this field of research.

Typically, the large/giant MCE is observed in the material that undergoes first order magnetic phase transition. Large number of magnetic materials with large entropy change accompanied by a first order phase transition have been reported [1-3, 7]. Apart from MCE, the first order magnetic transition (FOMT) gives rise to various other functional properties of technological importance, such as magnetostrictive, magnetoresistance, shape memory effects etc. [8]. However, the first-order phase transition is usually accompanied by considerable thermal and/or magnetic hysteresis along with irreversibility, which is disadvantage for a magnetic refrigeration cycle [7, 9-11]. But some of them, especially rare-earth-based intermetallic compounds, have reversible large MCE along with a small hysteresis loss [12-15]. Therefore

it is desirable to search for rare-earth-based intermetallic materials that not only exhibit large reversible MCE but also have none or negligible thermal and field hysteresis loss.

The RT_2X_2 compounds, where R is rare earth intermetallic compounds (Gd, Tb, Dy, Ho etc.), T is transition metal, and X is Si/Ge, is an important class of materials, which exhibits a wide variety of interesting physical properties [16-19]. Depending on the constituent element or composition, various properties like superconductivity, magnetic ordering, heavy-fermion properties, valence fluctuation, large MCE, etc. are observed [16-19]. As Mn carries magnetic moment, (unlike many other T elements such as Co, Ni and Fe) and its magnetic states strongly depends on intraplanar Mn-Mn distances, the compounds with $T = \text{Mn}$ attract particular interests [16, 20]. It is also known that, only in the case where $T = \text{Mn}$ do they display long-range magnetic order, which, incidentally can exist even above 300 K. However, the rare earth lattice orders magnetically at lower temperatures. The RMn_2X_2 compounds crystallize in the ThCr_2Si_2 -type body centered tetragonal structure (with space group $I4/mmm$) [21, 22] with repeated layers of atoms stacked in the sequence $R-X-Mn-X-R$ [20, 23] along the c-axis (similar to $R_5(\text{Si, Ge})_4$, a family of well-known large MCE materials) [24]. These characteristics of RT_2X_2 compounds offer scopes for selection of the magnetic state—and therefore the MCE—by controlling the interlayer and intralayer distances between magnetic atoms.

Recently, some RT_2X_2 compounds have been observed to possess not only large MCE but also a small hysteresis loss around their ordering temperature [18, 19]. The magnetic structure of HoMn_2Si_2 material has been studied using neutron diffraction dates from the 1990s [25]. This compound exhibits the crystal structure of ThCr_2Si_2 type with the Z parameter of Si in 4(e) site (space group $I4/mmm$). It exhibits antiferromagnetic ordering in the form of a flat spiral of Ho moments. Mn magnetic moments located in planes normal to

the c-axis are coupled ferromagnetically, but moments in adjacent planes can be coupled either ferromagnetically or antiferromagnetically. They are aligned along the c axis.

In order to improve the application of magnetocaloric cooling, efforts have been paid to search for magnetic refrigerants in view of domestic or industrial applications near room temperature [1-7]. On the other hand, the research on systems exhibiting large MCEs at low temperature is also important due to their prospective application in the refrigeration for gas liquefaction of hydrogen and helium [26-28]. Magnetic refrigeration at liquid helium temperatures is indeed of interest especially in space, medical and other cryogenic applications [29]. Significant capital cost reduction can potentially be achieved with a magnetic hydrogen liquefier compared to conventional liquefiers. Magnetic refrigeration may allow hydrogen to be competitive as an alternative fuel source [30].

In this paper, for achieving a complete understanding of HoMn_2Si_2 material, a detailed investigation of the magnetic structure and magnetic phase transitions was presented. A large reversible MCE was observed, accompanied by a first order magnetic phase transition which is applicable for low temperature magnetic refrigeration. Characteristics of the magnetic transition, the origin of large MCE as well as its potential application in HoMn_2Si_2 were discussed.

2. Experimental details

Polycrystalline HoMn_2Si_2 sample was synthesised by an arc melting method under an argon atmosphere. The stoichiometric amounts of high purity Ho (99.9 %), Mn (99.9 %) and Si (99.99 %) were melted four times for homogeneity on a water-cooled copper hearth. Around 3% excess Mn was added to compensate the Mn evaporation during the melting. The as-cast samples were sealed in an evacuated quartz tube and annealed for 1 week at 800°C followed by furnace cooling. The sample was proved to be single phase with the body

centered tetragonal $ThCr_2Si_2$ type structure by x-ray powder diffraction experimental (XRD) which employs Cu K- α radiation. The Rietveld refinements were carried out using the Fullprof program. Magnetic measurements, including temperature dependent magnetization curves and magnetization-field loops were performed in the temperature range of 2-300 K and field range of 0 - 7 T using a SQUID Magnetic Property Measurement System (MPMS) from Quantum Design Inc., San Diego. Heat capacity measurements were conducted on a Quantum Design 14 T physical properties measurement system.

3. Results and discussion

A schematic of the crystal structure of $HoMn_2Si_2$ is provided in **Fig. 1** along with Rietveld refinement of x ray data. The sample is confirmed to be single phase with the body centered tetragonal $ThCr_2Si_2$ type structure (space group $I4/mmm$). The calculated lattice parameters at room temperature [a (Å) = 3.922, c (Å) = 10.444 and V (Å³) = 16.044] derived from the refinement are in good agreement with the reported values [25, 31]. There is small amount of second phase present in the sample. According to ref. 32, the peak around 32 degree of 2 theta may be ascribed to the presence of $Ho_4Si_3O_{12}$ phase [32].

The temperature dependence of the magnetization (M) in the temperature (T) range of 5–150K in an applied field of 500 Oe under zero field cooling (ZFC) and field cooling (FC) process, is shown in **Fig. 2**. Multiple phase transitions have been detected. Similar behaviors had been reported in the compound $TbMn_2Si_2$ [33]. A major magnetic phase transition occurs around 80 K where $HoMn_2Si_2$ seems to enter the magnetically ordered state from antiferromagnetic state (based on ref. 20 where it was reported that the interlayer antiferromagnetic state forms around $T_N = 453$ K). Further, two more minor anomalies are present around at ~ 15 K and at 3.5 K in the ZFC magnetization data. According to ref. 25, the transition at 15 K can be ascribed to the formation of a flat spiral of Ho moment. The

reflection of the transition at temperature 3.5 K may be attributed to the ordering of Ho^{3+} moments but a detailed study is warranted. In order to test if the coexistence of multiple phases occurs, we measured thermal hysteresis in magnetization as shown in the top inset of **Fig. 2**.

There exists a definite thermal hysteresis below 20 K which might suggest the presence of multiple magnetic phases or structures at low temperatures. This is also a generic feature associated with the first order magnetic transition (FOMT). Usually, smaller thermal hysteresis is expected in the case of a first order magneto-elastic transition [34], On the other hand, a huge thermal hysteresis is observed in the case of magnetic transition connected with a martensitic-like structural transition. For the present compound the observed thermal hysteresis is very small. Therefore, the thermal hysteresis observed in HoMn_2Si_2 compound suggests that the magnetic transitions are not connected with structural change, but simply an iso-structural volume change associated with the magnetic transitions. This statement is consistent with the conclusion derived based on the available neutron results in [25] where no structural changes have been detected below room temperature for HoMn_2Si_2 .

The inverse magnetic susceptibility, $1/\chi(T)$, was fitted with a modified Curie-Weiss law in the paramagnetic region 180–300 K (not shown) following the expression $1/\chi(T) = \chi_0 + C/(T - \theta_p)$ where χ_0 is the temperature independent term and θ_p is the Curie-Weiss temperature. The evaluated value of effective magnetic moment is $\mu_{\text{eff}} = 12.27\mu_B$ and $\theta_p = -64$ K suggestive of antiferromagnetic correlations. The observed μ_{eff} is larger than the moment of free Ho^{3+} which is $10.6\mu_B$, suggests that the magnetic interaction in this compound is not only due to the rare earth ion but also there are contributions from the moment on Mn and from the effects of spin polarization of conduction electrons which is termed as magnetic polaronic effect [35]. The magnetic polarons mainly arises in compounds

with strong s - f exchange. This value is in good agreement with the expected value;

$$\mu_{eff} = \sqrt{[\{\mu_{eff}(Ho^{3+})\}^2 + \{\mu_{eff}(Mn^{3+})\}^2 + \{\mu_{eff}(Mn^{4+})\}^2]} = 12.35\mu_B.$$

For the RMn_2X_2 systems, it is well accepted that the magnetic ordering of Mn moments persists to the temperature above 300 K while magnetic ordering on rare earth occurs at low temperatures. Based on the only available neutron results at 4.2 K, 80 K and 293 K [25] for $HoMn_2Si_2$, it can be assumed that the Mn sublattices moment already forms a antiferromagnetic structure along c -axis at 293 K where the magnetic peaks (111) and (113) are present. While the Ho sublattice moment forms an incommensurate magnetic structure only below 80 K with a doubled flat spiral due to the fact that at 80 K no satellite peaks are present at 80 K neutron pattern [25]. Based on the fact there are no detailed neutron results in hand, we can only assume that the transition at 15 K corresponds to the formation of incommensurate magnetic structure (see the inset of Figure 1 in ref. [25] where the intensity of peak (001 $\pm$) drops sharply). However, due to the strong interaction between the moment from rare earth sublattice and Mn sublattice as detected in $TbMn_2Si_2$ [33, 36] and $DyMn_2Si_2$ [37], it should be expected that both Ho-sublattice and Mn sublattice will contribute to all the three magnetic transitions. In order to get a fully understanding these magnetic phase transitions, a detailed neutron diffraction experiment at variable temperatures is needed.

Apart from the multiple magnetic transitions, another feature worth noting from **Fig. 2** is the occurrence of thermomagnetic irreversibility between the FC and ZFC magnetization data. It is clearly seen that the ZFC and FC curves above 15 K are completely reversible, whereas a distinct discrepancy between ZFC and FC curves appears below this temperature. This thermomagnetic irreversibility can be observed in many cases such as spin-glass systems, materials with competing magnetic interactions, and ferromagnetic materials with high anisotropy [38-40].

In order to explore thermomagnetic irreversibility, the magnetic hysteresis loop of HoMn_2Si_2 at 2 K is measured and presented in the bottom inset of **Fig. 2**. A hysteresis with coercive field of 0.05 T is observed, confirming the anisotropy of HoMn_2Si_2 at low temperature. For the materials with high anisotropy and low ordering temperature, the narrow domain walls could exist, thus resulting in a large pinning effect [40]. In ZFC mode, the domain walls are pinned, and the thermal energy is not strong enough to overcome the energy barriers. This leads to the lower magnetization. On the other hand, in FC mode, the magnetic domains are already oriented along the applied magnetic field direction. As the domain walls move more easily when the temperature increases and therefore the magnetization at low temperature is higher than that in ZFC mode. Considering the magnetic anisotropy, it is anticipated that the thermomagnetic irreversibility between ZFC and FC curves seen in HoMn_2Si_2 is likely attributed to the narrow domain wall pinning effect.

A set of magnetic isotherms were measured for HoMn_2Si_2 with the temperature range 2 to 40 K up to 5 T applied field as shown in **Fig. 3 (a)**. A negligible hysteresis is observed for all the temperature range which may confirm a reversible MCE for that compound. It is apparent that the magnetization tends to saturate for sufficiently high magnetic fields. However, the attained value at 2K (87 emu/g for 5 T) reaches only 31% of that expected for a complete alignment of the magnetic moments of Ho^{3+} ($10 \mu_B$), Mn^{3+} ($4 \mu_B$), and Mn^{4+} ($3.8 \mu_B$), which is equivalent to a magnetization of 280 emu/g.

As we know that the magnitude of MCE has a strong correlation with the nature of the corresponding magnetic phase transition. So it is important to understand the order of magnetic transition in HoMn_2Si_2 . The measured Arrott plot for the compound HoMn_2Si_2 is shown in **Fig. 3(b)**. The S-shaped nature of the Arrott plot denotes the negative sign of the

coefficient $c_2(T)$ in the Landau expansion of the magnetic free energy, confirming the characteristic of a first order magnetic transition according to Banerjee criterion [41].

Temperature dependence of the heat capacity C_p for HoMn_2Si_2 in the temperature range of 0.5 to 150 K is shown in the **Fig. 4**. Two major anomalies are observed at ~ 18 K and at 4 K respectively (see **Fig. 4(a)**) which are consistence with the magnetization data. We observed the sign of anomaly around 80 K in the heat capacity even it is not less obvious compared with the two at lower temperatures (at ~ 18 K and at 4 K). In general, the heat capacity of materials with a first order magnetic phase transition exhibits a fairly sharp peak near the transition temperature while a λ -type anomaly is present around transition temperature in materials with a magnetic phase transition of second order. The size and shape of heat capacity anomaly may also depend on the sample purity and homogeneity. The almost absence of anomaly around 80 K here may also be ascribed to the small sensitivity of the PPMS device and type of this particular transition as described in ref [42] where similar behaviours occur for $\text{La}_{0.75}\text{Y}_{0.25}\text{Mn}_2\text{Si}_2$ that a clear anomaly is detected for T_C but no obvious anomaly is present at T_{AF} .

Fig. 4 (b) draws the very low temperature heat capacity for the temperature range 0.5-3 K in order to confirm the presence of any more anomalies. No anomaly is observed at that temperature range. As we know that the total heat capacity is the total contributions from the electrons, $C_{el}(T)$, phonons, $C_{ph}(T)$, and magnons, $C_m(T)$. At lower temperature region the main contribution comes from the electrons and phonons. In order to estimate the electrons contribution to specific heat we use an equation described as:

$$C_P = \gamma T + \beta T^3 \quad (1)$$

where the first tem represents the contribution of electrons and second term comes from the contribution of phonons. γ is given by:

$$\gamma = \pi^2 k_B^2 N(E_F)/3 \quad (2)$$

Here, $N(E_F)$ is the electronic density of states at the Fermi level and k_B is the Boltzmann constant.

To estimate the value for γ , a plot of C_p/T versus T^2 at lower temperatures (≤ 12 K) is derived and shown in **Fig. 4(c)**. The estimated values for γ is equal to 99 mJ/mol K² and the Debye temperature, $\Theta_D = 157$ K respectively. The estimated γ leads to the estimate of density of states at the Fermi level as $N(E_F) = 8.4$ states/eV (using equation 2). Compared with the γ values and $N(E_F)$ derived for LaMn₂Si₂ ($\gamma=33$ mJ/mol K² and $N(E_F)=2.82$ states/eV atom) [42], YMn₂Si₂ ($\gamma=18$ mJ/mol K² and $N(E_F)=1.52$ states/eV atom) [42] and TbMn₂Si₂ ($\gamma=28$ mJ/mol K² and $N(E_F)=2.38$ states/eV atom) [36] compounds, this remarkable large γ value may be due to an enhanced electronic density of states at the Fermi level.

It is observed that there is an increase of C_p/T at lower temperature inset in **Fig. 4**. This increase at lower temperature can be ascribed to the contribution from the nuclear specific heat C_N that arises due to the splitting of the nuclear hyperfine levels as described for PrAl₂ in [43] where it was found that heat capacity becomes enhanced at $T < 4$ K. This increase of C_p/T here for HoMn₂Si₂ is consistent with the discovery of large nuclear specific heat C_N in some of the lanthanides. It is accepted that the interactions of the nuclear magnetic moments with the strong magnetic field produced by the 4f electrons at the sites of the nuclei contributes to the high nuclear specific heat (C_N) at low temperature.

The magnetic entropy $-\Delta S_M$ for the present compound HoMn₂Si₂ was calculated from the magnetization isotherm $M(H, T)$ curves in **Fig. 3 (a)** using an integral version of Maxwell's thermodynamic relation

$$\Delta S_M(T, H) = \int_0^H \left(\frac{\partial M(T, H)}{\partial T} \right)_H dH \quad (3)$$

The temperature dependence of $-\Delta S_M$ for HoMn_2Si_2 calculated from $M(H, T)$ data for different magnetic field variations up to 5 T is shown in **Fig. 5**. The maximum values of magnetic entropy change reach about 4.8 and 9 J/kg K for the field change of 3 and 5 T respectively. These obtained values are comparable to larger than those of some potential low temperature magnetic refrigerants such as $\text{Ho}(\text{Ni}_{1-x}\text{Fe}_x)_2$, GdCuSi and PrCo_2B_2 [44-46]. This large magnetocaloric effect is suitable for low temperature magnetic refrigeration. It is clear from **Fig. 5** that the ΔS_M peak broadens asymmetrically towards high temperature on increasing the applied magnetic field. Such a behaviour is observed in systems with first-order phase transitions [47], spin-flop transition [48] and spin fluctuations [49].

4. Conclusions

To summarize, three magnetic phase transitions have been detected in HoMn_2Si_2 below room temperature. An obvious magneto-history effect below 15 K is present which can be attributed to narrow domain wall pinning effect. First order nature of the transitions is revealed by Arrott plots. Large magnetic entropy change $\Delta S_M = -9$ J/kg-K is observed at 9 K with the application of 5 T magnetic field which is applicable for the low temperature magnetic refrigeration. The low temperature heat capacity has been analysed in details suggesting the presence of large nuclear specific heat contribution.

Acknowledgement

J. C. Debnath acknowledges the Alfred Deakin Postdoctoral Research Fellowship at Deakin University, Australia.

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Figure Captions:

Fig. 1. (left) A schematic of the crystal structure of HoMn_2Si_2 . The Ho atoms are coloured violet, the Mn are green and Si are silver. (right) The Rietveld refinement of the x ray powder diffraction data of HoMn_2Si_2 in $I4/mmm$ symmetry.

Fig. 2. The magnetic response of HoMn_2Si_2 Shows the magnetization at 500 Oe where magnetic transitions at 80 K, 15 K and 3.5 K are identified. The top inset shows the thermal hysteresis is visible in magnetization below 20 K. The bottom inset shows the magnetic hysteresis loop of the compound at 2 K in low magnetic field.

Fig. 3. (a) Magnetic field dependence of the magnetization for HoMn_2Si_2 in the temperature range of 2-40 K with applied field of 5 T. (b) The corresponding Arrott plots of M^2 versus H/M .

Fig. 4. Temperature dependence of heat capacity for HoMn_2Si_2 for the temperature range from 0.5 to 150 K. (a) Enlarge low temperature part to show more visible transitions. (b) Low temperature (0.5 to 3 K) heat capacity graph. (c) Shows C_p/T versus T^2 at temperatures below 12 K.

Fig. 5. Magnetic entropy changes of HoMn_2Si_2 calculated from magnetizations as a function of temperature for different magnetic field changes up to 5 T.

Fig. 1. Debnath et al.

Fig. 2. Debnath et al.

Fig. 3. Debnath et al.

Figure 4 Debnath et al.

Fig. 5. Debnath et al.