Thermomagnetic Properties and Magnetocaloric Effect of TmFe$_2$ Compound

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Abstract

We report on a theoretical study of thermomagnetic and magnetocaloric properties of TmFe$_2$. The magnetization, total heat capacity, total entropy and magnetocaloric effect, namely isothermal entropy change $\Delta S_m$ and adiabatic temperature change $\Delta T_{ad}$, are calculated for magnetic fields up to 8T and for temperatures up to 700 K. Mean-field analysis, within the two sublattice model, showed that TmFe$_2$ is a ferrimagnetic compound exhibiting a compensation point at $T_{comp}$=200K and a Curie temperature at $T_C$ = 550K. Direct and inverse MCEs are shown to take place in this ferrimagnetic compound. We have calculated direct MCE with maximum $|\Delta S_m|$ of 0.50 J/mole K at $T_C$, and an inverse MCE with maximum $|\Delta S_m|$ of 0.57 J/mole. K, for an applied field change of 8T. $|\Delta T_{ad}|$ has its maximum value of 5.57 K in an applied field change of 8T. i.e. a temperature drop of 0.70 K/T has been achieved. The calculated Arrott plots and the relation between $|\Delta S_m|$ and $M^2$ demonstrated that the magnetic phase transition in this compound is of the second order. The mean-field model proves its suitability for calculating the properties of the compound under study.

Keywords: Magnetocaloric Effect, Rare Earth Transition Metal Compounds, Mean-Field Theory.

1. Introduction

Many studies of the thermomagnetic properties and magnetocaloric effect have been reported for the rare-earth intermetallic compounds [1-4]. The unusual thermal and magnetic properties associated with the partially filled f shell of the rare-earth ion have made these compounds interesting materials for many experimental and theoretical investigations[5]. The RFe$_2$ compounds are interesting in themselves as the spin-exchange interactions are stronger than those in R$_2$Fe$_{17}$, R$_6$Fe$_{23}$, and RFe$_3$ compounds[6], which makes their Curie temperatures the highest ones. RFe$_2$ compounds exhibit strong magnetic anisotropy and huge magnetostriction [7-12]. Several studies e.g. thermal and magnetic properties have been reported on the heat capacity and the crystal field effects of TmFe$_2$ [13, 14]. The antiparallel coupling between the Tm and Fe sublattices leads to a ferrimagnetic arrangement[15]. The TmFe$_2$ compound crystallizes in the cubic MgCu$_2$-Type crystal structure of the space group Fd$_3$m[16]. In the present work, we present a calculation of the thermomagnetic and magnetocaloric properties using the two-sublattice molecular field theory[17, 18], namely, the temperature-dependence of magnetization, the magnetic specific heat and the magnetic entropy in the temperature range of 0-700K and applied fields up to 8T. Debye temperature $\Theta_D$ is calculated from the bulk and shear moduli [19]. The electronic heat capacity coefficient $\gamma_e$ is calculated from the density of states at Fermi energy $E_F$ using the full-potential linear augmented plane wave as implemented in the Wien2k [20]. The lattice and electronic heat capacities are dependent on Debye temperature[21, 22] and electronic heat capacity coefficient[23]. Subsequently they were used in calculating the total specific heat and total entropy. In this work, we calculate the magnetocaloric effect in crystalline TmFe$_2$ compound. No studies, up to our knowledge, have been done, experimentally or theoretically, on the magnetocaloric properties of this compound. However there are studies on calculating the MCE of other RFe$_2$ compounds with R = Er, Ho e.g. an experimental work on ErFe$_2$ [3, 24] and through a simple theoretical model [25]. ErFe$_2$ has been reported to have a ferrimagnetic structure with a compensation point near its $T_C$. However a non-collinear magnetic structure has been ascribed to this compound e.g.[24]. Arrott plots [26] can be calculated using the Landau and Lifshitz theory for phase transitions [27]. These plots are well-known to be used for distinguishing the type of magnetic phase transition e.g. first or second order transition, and for determining the Curie temperature. The $M^2$ versus H/M and the $M^2$ versus $\Delta S_m$ [28, 29] plots are calculated at several temperatures in the vicinity of the critical temperature, for different
magnetic fields, where \( H \) and \( M \) are the applied field and magnetization respectively. For example, Belove [30] showed that the positive slope of the \( M^2 \) versus \( H/M \) curves is an indicative of a second order phase transition, whereas the negative slope indicates the presence of a first order transition.

2. Model and analysis

2.1. Thermomagnetic properties

Using the two-sublattice molecular field theory (MFT), the total effective field of \( \text{Tm} \) and \( \text{Fe} \) sublattices in \( \text{TmFe} \) compound can be expressed, respectively, as follows:

\[
U = -J_R n_{FeR} \tag{1}
\]

The temperature dependence of each sublattice moment is determined by the Brillouin function[31]:

\[
-\gamma_R (T) \tag{3}
\]

\[
-\gamma_F (T) \tag{4}
\]

and \((0)\) (and \((0)\)) are the magnetic moments, in Bohr magneton \((\mu_B)\), of \( \text{R} \) ion (\( \text{F} \) ion) at temperatures \( T \) and 0 K, respectively. The MFT coefficients are \( n_R \), \( n_F \), and \( n_{RF} \). The factor converts the moments from to emu/cm\(^3\), where \( A \) is the formula weight. \( J_R \) and \( J_{RF} \) are the individual angular momenta of \( \text{R} \) and \( \text{F} \), respectively. The resultant magnetization is given by:

\[
M_F (T) = n_{FeR} \gamma_F (T) \tag{5}
\]

In order to calculate the magnetic specific heat, we start off with the magnetic energy of a binary magnetic compound

\[
U = -J_R n_{FeR} \tag{6}
\]

The magnetic specific heat is determined by:

\[
-\gamma_F (T) \tag{7}
\]

The magnetic entropy can be calculated from the numerical integration of the magnetic heat capacity as follows:

\[
-\gamma_F (T) dT \tag{8}
\]

The total heat capacity at constant pressure \( C_{total} \) includes three contributions, namely, the lattice heat capacity \( C_l \), the electronic heat capacity \( C_e \) and the magnetic heat capacity \( C_m \):

\[
C_{total} = C_l + C_e + C_m \tag{9}
\]

The lattice heat capacity is expressed as:

\[
C_l = 9 R \{ 4 (-)^2 \} \tag{10}
\]

Where \( \theta_D \) shows that the positive slope of the \( M \) versus \( T \) and \( \theta_D \) is Debye temperature which can be calculated using the following relation[32]:

\[
\theta_D = \Omega / T \tag{11}
\]

where \( \Omega \) is Planck’s constant, \( k_B \) is the Boltzmann constant, \( N_A \) is the Avogadro number, \( \gamma \) is the density, \( A \) is the molecular weight, \( v_m \) is the average sound velocity, and \( n \) is the number of atoms per formula unit.

The average sound velocity in the polycrystalline material is given by[33]:

\[
v_m = \left[ -\gamma_R (T) - \gamma_F (T) \right]^{1/3} \tag{12}
\]

where \( \gamma_R \) and \( \gamma_F \) are the longitudinal and transverse sound velocities respectively, which can be obtained using the shear and the bulk moduli \( G \) and \( B \), from Navier’s equation, respectively [34]:

\[
\sqrt{-\gamma_R} and \sqrt{-\gamma_F} \tag{13}
\]

The electronic contribution to heat capacity is proportional to \( T \) at any temperature. Taking into account the Fermi-Dirac statistics of electrons in metals and their band structure, the electronic heat capacity is given by:

\[
C_e = -k_B^2 D(E_F) T = \gamma_e T \tag{14}
\]

where \( \gamma_e = \pi^2 k_B^2 D(E_F)/3 \) is the electronic heat-capacity coefficient, and \( D(E_F) \) is the electron density of states at the Fermi energy \( E_F \).

Generally speaking, the total entropy of a magnetic material is made up of the contributions from the crystalline lattice \( S_l \), from the conduction electrons \( S_e \), and from the atomic magnetic moments \( S_m \). The total entropy can be calculated from the numerical integration of the total heat capacity:

\[
S_T = \int C(T) dT \tag{15}
\]

The lattice part is given by:

\[
S_L = 3 R \{ 4 (-)^2 \} \ln [ ] \tag{16}
\]
2.2. Magnetocaloric Effect

The MCE is intrinsic to all magnetic materials and is induced via the coupling of magnetic lattice with the applied magnetic field. The MCE is identified through two distinguishing parameters namely: the adiabatic temperature change and the isothermal entropy change. In an isothermal process, the entropy change upon magnetic field variation from $H_1$ to $H_2$, in compounds undergoing a second order phase transition, is calculated from the following Maxwell relation [35] as shown:

$$ -\Delta S = -(3J/2J+1)N\sigma_0(\sigma^2 - \sigma_{\text{spont}}^2) $$

Where $\sigma = Mg\mu_B N$ is the reduced magnetization, $\sigma_{\text{spont}}$ is the spontaneous magnetization, $J$ is the angular momentum, and $N$ is the number of spins.

3. Results and discussion

3.1. Magnetization

The temperature dependence of magnetization of the rare-earth and Fe sublattices, as well as the total magnetization for TmFe$_2$, are calculated by using the two-sublattice molecular field theory. The total magnetization, at $T=0$ K, is 3.72 $\mu_B$/F.U. in fair agreement with available theoretical and experimental values as reported by Y. Tang et al [6] Clark et al [9] respectively. Fig. 1 displays the temperature dependence of magnetization, in zero field. It is clear that a ferrimagnetic-paramagnetic phase transition occurs at $T_c$=550 K, in addition to a compensation point at $T=225$ K. The temperature dependence of the magnetization in external magnetic fields of $H=0$, 4, and 8 T is shown in Figs. 2-3. The behavior shown in these two figures is consistent with that reported by P. Von Ranke [25] for a ferrimagnetic compound. The compensation temperature $T_{\text{comp}}$ decreases from 225 K to 190 K almost linearly with increasing the magnetic field as shown in Fig. 4. It may be mentioned here that some RFe$_2$ compounds, e.g. ErFe$_2$, has been reported to have a ferrimagnetic structure with a compensation point near its $T_c$. However a non-collinear magnetic structure has been suggested for this compound e.g. [24]. It is known, for comparison, that some amorphous rare-earth iron compounds e.g. Dy-Fe have a sperimagnetic structure [36]. In addition Chaaba et al [24], have reported on the possibility of a field-induced non-collinear structure in ErFe$_2$. We cannot, to our knowledge and in the absence of neutron diffraction data or specific magnetic measurements on TmFe$_2$, to confirm or exclude a possible non-collinear structure in this compound.

3.2. Heat capacity

It is necessary to calculate the total heat capacity under the action of an applied magnetic field to provide some insight into the thermomagnetic characterization of the TmFe$_2$ material. To calculate the total heat capacity for TmFe$_2$, three contributions should be calculated as we mentioned before in Eq. (9). The magnetic heat capacity part is calculated from the sum of the four different sublattice contributions: Fe-Fe, Fe-Tm, Tm-Tm and Tm-Fe. Fig. 5 shows that the magnetic heat capacity has value equal to 33 J/K.mole at zero field. The largest contribution is that of the Fe-Fe interaction, and the Tm-Tm intra-sublattice interaction has the least contribution. Fig. 6 displays the field-dependence of the magnetic specific heat as a function of temperature. The maximum magnetic heat capacity decreases by increasing the applied field.
around $T_C$ which is typical for ferrimagnetic compounds\cite{16}. We have calculated the coefficient $\gamma_e$, from the density of states at $E_F$ and obtained a value of 12 mJ/K$^2$-mole which is consistent with 14 mJ/K$^2$-mole [37]. The electronic heat capacity is then determined by eq. 14. $\Theta_0$ is calculated from the mean sound velocity, as shown in eqs. (11- 14). The bulk and shear moduli are 190.65 and 60.18 GPa respectively. They were calculated by statistical-learned-based predictions\cite{38} as reported by material projects\cite{39}. The calculated $\Theta_0$ is 330K with a percentage difference less than 10% compared to the experimental value 301K\cite{37}. Our result of the total heat capacity, in zero and different applied fields, is shown in Fig. 7, which illustrates a weak dependence of heat capacity on the applied field at low temperatures, however the field dependence increases around $T_c$.

3.3. Total entropy

The entropy is calculated from the heat capacity using Eq. (15). Fig. 8 illustrates the magnetic entropy and its sublattice contributions in zero field. The total magnetic entropy saturates, at $T=T_c$ to about 36.4 J/K-mole. The largest contribution to magnetic entropy is that of the Fe-Tm interaction. The calculated magnetic entropy at 0, 4 and 8T shows that the magnetic entropy increases upon increasing the applied field Fig. 9. The increase in the magnetic entropy could be because of the non-collinear property which has been reported in some RFe$_2$-compounds, especially compounds with a compensation point in their temperature dependence of magnetization e.g. ErFe$_2$ [3, 24]. It could be mentioned that a deformation in the antiferromagnetic (AFM) structure of elemental Tm, and a subsequent increase in magnetic entropy, upon applying a magnetic field, has been reported by Tishin [40]. Fig. 10 shows that the magnetic entropy for Fe-Tm interaction, has the highest contribution, which increases with increasing the applied field. The magnetic entropy for Fe-Fe and Tm-Fe sublattices decreases with increasing the applied field, however the entropy field-dependence of Tm-Tm and Fe-Tm sublattices is opposite. The behavior just explained leads to increasing the magnetic and total entropy slightly with the magnetic field as in Fig. 11.

3.4. Magnetocaloric effect

Fig. 12 shows the isothermal entropy change for magnetic field values from 0 to 8 T. The curve, at different fields, exhibit two peaks: the first one occurs at temperature around 95 K, which is below the compensation temperature (\sim 220 K). The second, rather smaller peak, has its maximum at the ferrimagnetic-paramagnetic phase transition at $T_c$=550 K. The main features in Fig. 12 are consistent with those reported for ferrimagnetic compounds e.g. ErFe$_2$ [24, 3] and HoFe$_2$[3]. Fig.13 shows the first temperature-derivative of magnetization ( $M/ T$) for the same fields used in Fig.12. It is clear that the main features of the two figures e.g. the temperature and magnetic field dependence are the same. Fig. 14 shows $\Delta T$ for the same magnetic field changes as in Fig.12. The maximum values are: 2.01, 3.51, 4.62 and 5.57 K for applied field changes of 2, 4, 6 and 8 T respectively. We calculated $\Delta T$ using Eq.(20), because of the weak dependence of the total heat capacity on the applied field as shown in Fig. 15. Namely the presence of a weak dependence of $T/C_{rot}$ on the applied field within the temperature range up to $T_c$. For $T> T_c$, a rather weak field-dependence is found. The data of the magnetocaloric effect is tabulated in Tables 1 and 2. We notice that the maximum value for $\Delta T$ is 5.60K for applied field 8T i.e. the temperature is decreasing by 0.70K/T. Figs. 16-17 show Arrott plots and the relationship between $M$ and $\Delta T$ in the temperature range 500 - 560 K, around $T_c$, for applied fields of 0.1, 2, 3.5 and 7T. These plots show positive slopes, which confirm a second order phase transition. The curve starting from the origin represents the data at $T_c$=550K. This is consistent with temperature dependence of magnetization. e.g. Fig. 1.

4. Conclusions

We have calculated the thermomagnetic properties for TmFe$_2$ using the two sublattice molecular field model and standard formulae for the lattice and electronic heat capacities and entropies. Magnetization calculation has shown that TmFe$_2$ is ferrimagnetic with a compensation point of $T_{comp}$=225K and a Curie temperature close to 550 K. The magnetic specific heat and magnetic entropy, in different magnetic fields between 0 and 8 T, showed that the phase transition involved in these compounds is of the second type. Furthermore, the contribution of the Fe-Tm exchange interaction to the magnetic entropy is probably the main reason for increasing the entropy upon increasing the applied field. The bulk and shear moduli are 190.65 and 60.18 GPa respectively. We have used these values for calculating $\Theta_0$ which is around 330K. Using the density of states at $E_F$, we calculated $\gamma_e$ to be around 12 mJ/K$^2$-mole. Subsequently, we have used $\Theta_0$ and $\gamma_e$ to calculate the lattice and electronic entropies respectively. Both ordinary and inverse magnetocaloric effect are present for the compound. The highest ordinary is around 0.50 J/mol.K at $T_c$= 550 K and the highest inverse is - 0.57 J/mol.K for a magnetic field change of 8T. The adiabatic temperature change per tesla is 0.70 K/T. Arrott plots and the $M^2$ relations have supported our conclusion concerning the type of the phase transition in these compounds i.e. second order phase transition. The $T_c$ value calculated from Arrott plots is fairly close to that calculated from the temperature dependence of magnetization. We may conclude that the magnetocaloric effect in TmFe$_2$ is relatively consistent with the MCE of, for example, ErFe$_2$, which has the same features of the temperature dependence of magnetization as TmFe$_2$. The mean-field analysis proved to be suitable for calculating the magnetothermical and magnetocaloric properties of the
compound studied. Further investigations of a possible non collinear magnetic structure in this compound are suggested.

5. References


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Fig. 15. The dependence of $T/C_{\text{total}}$ on temperature in H=0, 4 and 8 T.

Fig. 16. Arrott plot for applied magnetic fields from 0 to 7 T at various temperatures.
$S_M$ vs $M^2$ plot for applied fields of 0-7 T at various temperatures.  

Fig. 17.
### Table 1: The values of direct magnetocaloric effect ($\Delta S_m$) and (-\(\Delta T\)) at \(T_c\), for different field changes.

<table>
<thead>
<tr>
<th>(T_c) (K)</th>
<th>(\Delta H(T))</th>
<th>(\Delta S_m) (J/K.mole)</th>
<th>(-\Delta T) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>555</td>
<td>2</td>
<td>0.202</td>
<td>2.26</td>
</tr>
<tr>
<td>557</td>
<td>4</td>
<td>0.313</td>
<td>3.54</td>
</tr>
<tr>
<td>560</td>
<td>6</td>
<td>0.406</td>
<td>4.62</td>
</tr>
<tr>
<td>563</td>
<td>8</td>
<td>0.500</td>
<td>5.57</td>
</tr>
</tbody>
</table>

### Table 2: The values of \(T_{\text{comp}}\) and inverse magnetocaloric effect (\(\Delta S_m\)) and (\(\Delta T\)) for different field changes.

<table>
<thead>
<tr>
<th>(T_{\text{comp}}) (K)</th>
<th>(\Delta H(T))</th>
<th>(-\Delta S_m) (J/K.mole)</th>
<th>(\Delta T) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
<td>2</td>
<td>0.132</td>
<td>0.90</td>
</tr>
<tr>
<td>215</td>
<td>4</td>
<td>0.260</td>
<td>1.66</td>
</tr>
<tr>
<td>206</td>
<td>6</td>
<td>0.440</td>
<td>2.73</td>
</tr>
<tr>
<td>200</td>
<td>8</td>
<td>0.577</td>
<td>3.73</td>
</tr>
</tbody>
</table>