Thermomagnetic Properties and Magnetocaloric Effect of \(R_2Fe_{17}C\) (\(R=\)Dy, Nd, Tb, Gd, Pr, Ho, Er) Compounds

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Abstract: We present a mean-field analysis, using the two-sublattice model, for the thermomagnetic and magnetocaloric properties of the \(R_2Fe_{17}C\) compounds, where \(R=\)Dy, Nd, Tb, Gd, Pr, Ho, Er and C is carbon. The dependence of magnetization, magnetic entropy, magnetic entropy and isothermal entropy change \(\Delta S_m\), are calculated for magnetic fields up to 5 T and for temperatures up to 700 K. Direct magnetocaloric effect is present for all compounds with maximum \(\Delta S_m\) between 6.13-10.95 J/K.mol for an applied field change of 5T. It is found that \(Pr_2Fe_{17}C\) compound has the highest \(\Delta S_m\) of 10.95 J/K.mole at \(\Delta H=5T\) and \(T_c=375\) K. The inverse MCE is found in ferrimagnetic compounds, e.g. \(Gd_2Fe_{17}C\), with \(\Delta S_m=6.13\) J/K mol at critical temperature \(T_c=623\) K and \(\Delta S_m=0.12\) J/K mol at Neel temperature \(T_N=136\) K. The calculated Arrott plots confirmed that the magnetic phase transitions in these compounds are of second order. The mean-field model proves its suitability for calculating the properties of the compounds under study.

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

1 Introduction

In the course of search for new permanent magnetic materials, several studies have been reported on using the two-sublattice molecular field model for calculating the magnetic properties of the rare-earth Fe-rich system \(R_2Fe_{17}C\)[1]. The \(R_2Fe_{17}C\) compounds crystallize in the rhombohedral \(Th_2Zn_{17}\)-Type crystal structure of the space group \(P6_3/mmc\)[2]. No studies, up to our knowledge, have been done, experimentally or theoretically, on the magnetocaloric properties of these alloys.

In the present work, we focus our efforts on calculating magnetic properties of \(R_2Fe_{17}C\), where \(R\) stands for Nd, Pr, Gd, Er, Dy, Tb and Ho, such as: the temperature-dependence of magnetization, magnetic specific heat, magnetic entropy and magnetocaloric effect, \(\Delta S_m\) using the two-sublattice molecular field theory MFT [3,4].

The magnetic specific heat can be calculated from the differentiation of the magnetic energy with respect to temperature. Also, the magnetic entropy could, then, be calculated by numerically processing the magnetic specific heat data in a certain range of temperatures and magnetic fields. Using the Landau and Lifshitz theory for phase transitions[5,6], we can calculate the Arrott plots [7] which are used in determining the nature of the ferromagnetic phase transition and in estimating the critical temperature. The \(M^2\) versus \(H/M\) and the \(M^2\) versus \(\Delta S_m\) [8,9] 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. Belove [10] 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 [10,11].

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2 Model and analyses

Using the two-sublattice molecular field theory MFT, we will calculate, first, the temperature-dependence of magnetization M(T). The total effective field of R and Fe sublattices in $R_2Fe_{17}$C compounds can be expressed, respectively, as follows:

$$H_R(T) = H + d[2 n_{RR} M_R(T) + 17 n_{RF} M_F(T)]$$

$$H_{Fe}(T) = H + [17 n_{FF} M_F(T) + 2 n_{FR} M_R(T)]$$

where H is the external field in A/m in the SI system of units. The temperature dependence of each sublattice moment is determined by the Brillouin functions[12,13]:

$$M_R(T) = M_R(0) B_{JR} \left[ \frac{M_R(0) H_R(T)}{KT} \right]$$

$$M_{Fe}(T) = M_{Fe}(0) B_{JF} \left[ \frac{M_{Fe}(0) H_{Fe}(T)}{KT} \right]$$

$M_R(T)$ and $M_R(0)$ ($M_{Fe}(T)$ and $M_{Fe}(0)$) are the magnetic moments, in Bohr magneton $\mu_B$, of R ion (Fe ion) at temperatures $T$ and 0 K, respectively. The MFT coefficients are $n_{RF}$, $n_{RR}$ and $n_{FR}$. In our calculation, these MFT coefficients are from the work of Wu et al [1]. The factor $d = N_A \mu_B \phi/A$ converts the moments per unit volume from $\mu_B$ to A/m, where $\phi$ is the density of $R_2Fe_{17}$C in kg/m$^3$, $N_A$ is the Avogadro's number and A is the formula weight of $R_2Fe_{17}$C in kg. $J_R$ and $J_{Fe}$ are the individual angular moments of R and Fe, respectively. The resultant magnetization is given by

$$M_{tot}(T) = [2 M_R(T) + 17 M_{Fe}(T)]$$

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

$$U = -\frac{1}{2} n_{RR} M_R^2(T) + n_{FF} M_F^2(T) + 2 n_{RF} M_R(T) M_{Fe}(T)$$

The magnetic specific heat is determined by:

$$C_m(T) = \left( \frac{\partial U}{\partial T} \right)_H$$

and the magnetic entropy is calculated from:

$$S_m(T) = \int_{T1}^{T2} C_m(T) \frac{dT}{T}$$

Both of the specific heat and entropy are in units of J/K mole.

The isothermal magnetic entropy change can be calculated in two ways:

i) Direct subtraction of the entropies at two different fields but at the same temperature i.e.:

$$\Delta S_m(T, \Delta H) = S_m(T, H_2) - S_m(T, H_1) \quad H_2 > H_1$$

ii) Using the Maxwell relation:

$$\Delta S_m(T, \Delta H) = \int_{H1}^{H2} \left( \frac{\partial M_{tot}(T,H)}{\partial T} \right)_H dH$$

Arrott plots are calculated in accordance with the equation of state [14]

$$\frac{H}{M} = \frac{(T-T_C)}{T_1} + \left( \frac{M}{M_1} \right)^2$$

where $T_1$ and $M_1$ are set of adjustable parameters

It’s remarked that $\Delta S_M$ is proportional to $M^2$ from the mean field model [8,9], so

$$\Delta S_{M(\sigma)} = \frac{3J}{2J+1} N k_B (\sigma^2 - \sigma^2_{spont})$$

269
where $\sigma$ is the magnetization per unit mass.

3 Results and discussion

3.1 Magnetization

The total magnetization, as function of temperature, and in zero field, for all the compounds under study is shown in Fig.1. The total magnetization, at T=0 K, is the largest for Pr$_2$Fe$_{17}$C and Nd$_2$Fe$_{17}$C namely: 32.27 and 28.64 $\mu_B/\text{f.u.}$ (see table 1) respectively. Figs 2 and 3 show the temperature dependence of magnetization of the rare-earth and Fe sublattices as well as the total magnetization for the Nd$_2$Fe$_{17}$C, Pr$_2$Fe$_{17}$C and Gd$_2$Fe$_{17}$C. It is evident that the intra-sublattice interaction of the iron sublattice is the largest one. This is due to that the number of iron atoms involved in this compounds is greater than that of rare earth atoms.

Figure 1. The total magnetization for R$_2$Fe$_{17}$C compounds where R=Dy, Er,Gd,Ho, Nd,Pr and Tb.

Figure 2. The net magnetization for each sublattice vs temperature for ferromagnetic Pr$_2$Fe$_{17}$C.

Figure 3. The net magnetization for each sublattice vs temperature for ferromagnetic Nd$_2$Fe$_{17}$C.

Figure 4. The net magnetization for each sublattice vs temperature for ferrimagnetic Gd$_2$Fe$_{17}$C.
3.2 Magnetic heat capacity and entropy

The different sublattice contributions to the magnetic specific heat of Pr$_2$Fe$_{17}$C, at zero field, are shown in Fig(5). The largest contribution is that of the Fe-sublattice. Figure (6) displays the field-dependence of the magnetic specific heat of the same compound as a function of temperature. This behavior is typical for ferromagnetic compounds[1].

![Figure 5](image1.png)  ![Figure 6](image2.png)

**Figure 5.** The different inter and intra sublattice contributions to the magnetic specific heat: Fe-Fe, Fe-Pr, Pr-Pr and Pr-Fe, at zero magnetic field, as a function of temperature for the Pr$_2$Fe$_{17}$C compound.

**Figure 6.** The Total magnetic specific heat in H=0, 5 and 10T for the Pr$_2$Fe$_{17}$C compound.

Figures(7, 8) illustrate the total entropy and its sublattice contributions, in zero field, for Er$_2$Fe$_{17}$C and Gd$_2$Fe$_{17}$C respectively. The total entropy saturates, at T=T$_c$ to about 200 and 190 J/K.mole for these two compounds respectively. The largest contribution to magnetic entropy is that of the Fe-Fe interaction, whereas the other three interactions contribute only about 25% to the total magnetic entropy. The calculated total magnetic entropy at 0 and 10 T for Pr$_2$Fe$_{17}$C (Gd$_2$Fe$_{17}$C) compound is shown in figs. 9(10). Table 1, displays the calculated total magnetization, magnetic entropy and magnetic specific heat data at zero temperature and magnetic field for all compounds. The shown field-dependence of magnetic entropy, at a given temperature, reflects the role of magnetic field in aligning the moments and hence reducing the magnetic entropy[14].

**Table 1:** The values of T$_c$, magnetization M, magnetic specific heat C$_m$ and magnetic entropy S$_m$ for R$_2$Fe$_{17}$C compound in zero applied field.

| System R | T$_c$ (K) | Calculated Max C$_m$ H=0 T (J/K.mole) | Max S$_m$ H=0 T (J/K.mole) | Magnetization at T=0 $10^3$ (A/m) |
|----------|-----------|-------------------------------------|--------------------------|-------------------------------|
| Pr       | 375       | 32.274                              | 189.65                   | 345.83                        |
| Nd       | 455       | 28.646                              | 191.52                   | 355.32                        |
| Ho       | 502       | 16.754                              | 200.15                   | 359.28                        |
| Er       | 506       | 17.530                              | 199.47                   | 342.40                        |
| Dy       | 559       | 14.935                              | 200.08                   | 324.74                        |
| Tb       | 568       | 17.887                              | 195.91                   | 378.87                        |
Figure 7. The calculated magnetic entropy contributions for Fe-Fe, Fe-Er, Er-Er and Er-Fe interactions at zero magnetic field as a function of temperature for Er\textsubscript{2}Fe\textsubscript{17}C.

Figure 8. The calculated magnetic entropy contributions for Fe-Fe, Fe-Er, Er-Er and Er-Fe interactions at zero magnetic field as a function of temperature for Gd\textsubscript{2}Fe\textsubscript{17}C compound.

Figure 9. The calculated total magnetic entropy at zero magnetic field and H=10T as a function of temperature for Pr\textsubscript{2}Fe\textsubscript{17}C.

Figure 10. The calculated total magnetic entropy at zero magnetic field and H=10T as a function of temperature for Gd\textsubscript{2}Fe\textsubscript{17}C.

3.3 Magnetocaloric effect

We have calculated the magnetocaloric effect $\Delta S_m(T, \Delta H)$ by using two different methods, as mentioned before, e.g. using either Eq.9 or 10. The temperature dependence of the magnetic entropy change, using Eq.9, for R\textsubscript{2}Fe\textsubscript{17}C where R= Pr, Nd, Tb, Dy, Ho, Gd and Er in magnetic field changes of 1, 2, 3 and 5T, are shown in Figs. (11-17).
Figure 11. Isothermal entropy change vs T in ferromagnetic Pr$_2$Fe$_{17}$C compound for applied magnetic fields from 1 to 5 T.

Figure 12. Isothermal entropy change vs T in ferromagnetic Nd$_2$Fe$_{17}$C compound for applied magnetic fields from 1 to 5 T.

Figure 13. Isothermal entropy change vs T in ferrimagnetic Dy$_2$Fe$_{17}$C compound for applied magnetic fields from 1 to 5 T.

Figure 14. Isothermal entropy change vs T in ferrimagnetic Er$_2$Fe$_{17}$C compound for applied magnetic fields from 1 to 5 T.
Figure 15. Isothermal entropy change vs T in ferrimagnetic Gd$_2$Fe$_{17}$C compound for applied magnetic fields from 1 to 5 T.

Figure 16. Isothermal entropy change vs T in ferrimagnetic Ho$_2$Fe$_{17}$C compound for applied magnetic fields from 1 to 5 T.

Figure 17. Isothermal entropy change vs T in ferrimagnetic Tb$_2$Fe$_{17}$C compound for applied magnetic fields from 1 to 5 T.

$\Delta S_M(T, \Delta H)$ has maximum values of $\approx 2.85, 5.18, 7.25$ and $10.95$ J/mole K for Pr$_2$Fe$_{17}$C (fig.11). Inverse magnetocaloric values of $1.5, 2.87, 4.06$ and $6.13$ J/K.mole are calculated for Gd$_2$Fe$_{17}$C The data for the magnetocaloric effect is provided in Tables 2 and 3.
Table 2: The values of magnetocaloric effect (- $\Delta S_m$) at different applied fields from 0 to 5T

| System R | Tc Calculated (K) | $-\Delta S_M$ $\Delta H=1T$ (J/K.mole) | $-\Delta S_M$ $\Delta H=2T$ (J/K.mole) | $-\Delta S_M$ $\Delta H=3T$ (J/K.mole) | $-\Delta S_M$ $\Delta H=5T$ (J/K.mole) |
|----------|-------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| Pr       | 375               | 2.85                                 | 5.18                                 | 7.25                                 | 10.95                                |
| Nd       | 455               | 3.14                                 | 5.18                                 | 6.93                                 | 10.01                                |
| Ho       | 502               | 1.92                                 | 3.25                                 | 4.34                                 | 6.12                                 |
| Er       | 506               | 2.35                                 | 3.61                                 | 4.56                                 | 5.96                                 |
| Dy       | 558               | 2.08                                 | 3.32                                 | 4.32                                 | 5.98                                 |
| Tb       | 568               | 1.94                                 | 3.23                                 | 4.37                                 | 6.15                                 |
| Gd       | 623               | 1.50                                 | 2.87                                 | 4.06                                 | 6.13                                 |

Table 3: The values of the inverse magnetocaloric effect $\Delta S_m$ at different applied fields from 0 to 5T.

| System R | $T_N$ (K) | $\Delta S_M$ $\Delta H=1T$ (J/K.mole) | $\Delta S_M$ $\Delta H=2T$ (J/K.mole) | $\Delta S_M$ $\Delta H=3T$ (J/K.mole) | $\Delta S_M$ $\Delta H=5T$ (J/K.mole) |
|----------|-----------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| Gd       | 136       | 0.023                                | 0.047                                | 0.074                                | 0.12                                 |
| Tb       | 140       | 0.10                                 | 0.19                                 | 1.44                                 | 0.51                                 |
| Er       | 150       | 0.65                                 | 1.33                                 | 2.04                                 | 3.45                                 |
| Ho       | 152       | 0.33                                 | 1.033                                | 1.03                                 | 1.64                                 |
| Dy       | 160       | 0.23                                 | 0.66                                 | 1                                    | 1.15                                 |

For the sake of comparison between the results of the two methods used for calculating $|\Delta S_M(T,\Delta H)|$, we display them in fig.18 for R=Dy. It is clear that the results of the two methods are rather similar, however the maximum value of $\Delta S_M(T,\Delta H)$ is relatively higher for the direct subtraction method.

Figure 18. Isothermal entropy change vs T for Dy$_2$Fe$_{17}$C compound for applied magnetic field 1T by using two methods.
It is clear from using Maxwell relation that Pr$_2$Fe$_{17}$C and Nd$_2$Fe$_{17}$C ferromagnetic materials have the highest $\Delta S_M$ values at $T_c = 380$ K and 455 K respectively (Fig.19) for an applied fields from 1 to 5 T. Fig.20 displays the magnetization first-derivative with respect to temperature. The maximum values of this derivative is the integrand in eq.10.

**Figure 19.** the maximum Isothermal entropy change vs T in R$_2$Fe$_{17}$C compounds for applied magnetic fields from 1 to 5 T.

**Figure 20.** the temperature first-derivative of magnetization for R$_2$Fe$_{17}$C compounds at applied magnetic field = 5 T.

Arrott plots are calculated for Pr$_2$Fe$_{17}$C and Gd$_2$Fe$_{17}$C as shown in Figs.21 and 22. These plots show that positive slopes are obtained for applied fields of 1, 2, 3 and 5 T at temperatures around $T_c$, which confirms a second order phase transition[10] for Gd$_2$Fe$_{17}$C and Pr$_2$Fe$_{17}$C.

**Figure 21.** Arrott plot in ferrimagnetic Gd$_2$Fe$_{17}$C compound for applied magnetic fields from 0 to 5 T at various temperatures.

**Figure 22.** Arrott plot for ferromagnetic Pr$_2$Fe$_{17}$C compound for applied magnetic fields from 0 to 5 T at different temperatures.
Figures (23) and (24) indicate that the relationship between \( \Delta S_M \) and \( M^2 \) is linear for \( \text{Nd}_2\text{Fe}_{17}\text{C} \) and \( \text{Gd}_2\text{Fe}_{17}\text{C} \) compounds where the line passes through the origin at \( T_c = 455 \) K and \( 623 \) K respectively.

**Figure 23.** \( \Delta S_M \) vs \( M^2 \) plot for \( \text{Gd}_2\text{Fe}_{17}\text{C} \) compound at applied fields of 1-8 T.

**Figure 24.** \( \Delta S_M \) vs \( M^2 \) plot for \( \text{Nd}_2\text{Fe}_{17}\text{C} \) compound at applied fields of 1-8 T.

### 4 Conclusions

Thermomagnetic properties have been calculated for \( \text{R}_2\text{Fe}_{17}\text{C} \); \( \text{R} = \text{Nd}, \text{Pr}, \text{Gd}, \text{Er}, \text{Dy}, \text{Tb} \) and \( \text{Ho} \) using the two sublattice molecular field theory. Magnetization calculation have shown that the compounds \( \text{Pr}_2\text{Fe}_{17}\text{C} \) and \( \text{Nd}_2\text{Fe}_{17}\text{C} \) are ferromagnetic while the other compounds are ferrimagnetic. The magnetic specific heat and the magnetic entropy at different magnetic fields between 0 and 5 T showed that the phase transition involved in these compounds is of the second type. Furthermore, the contribution of the Fe-Fe exchange interaction to the magnetic entropy and heat capacity is the highest compared to other sublattice interactions.

Arrott plots and the \( \Delta S_M \) vs. \( M^2 \) relations have supported our conclusion concerning the type of the phase transition in these compounds i.e. second order phase transition. The \( T_c \) values calculated from Arrott plots are fairly close to those calculated from the temperature dependence of magnetization. Both ordinary and inverse magnetocaloric effect are present for all the compounds except those with \( \text{R}=\text{Nd} \) and \( \text{Pr} \), where only direct \( \Delta S_M \) is present. The highest ordinary \( \Delta S_M \) is calculated for \( \text{R}=\text{Pr} \) around 11 J/mol.K at \( T_c = 375 \) K and the highest inverse \( \Delta S_M \) of 3.45 J/mol.K is calculated for \( \text{R}=\text{Er} \) for a 5T magnetic field change. The magnetocaloric effect \( \Delta S_M \) has been determined using two methods i.e. the direct subtraction and using Maxwell relation. The two methods nearly produce the same temperature dependence except that the direct-subtraction method yields a relatively higher \( \Delta S_M \) at \( T_c \).

We may conclude that the magnetocaloric effect in these materials is relatively high in particular for \( \text{R}=\text{Pr} \), which has a Curie temperature not very far from room temperature. The mean-field analysis proved to be suitable for calculating the magnetothermal and magnetocaloric properties of the compounds studied.
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