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Citation: Appl. Phys. Lett. 100, 242408 (2012); doi: 10.1063/1.4729122
View online: http://dx.doi.org/10.1063/1.4729122
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Normal or inverse magnetocaloric effects at the transition between antiferromagnetism and ferromagnetism

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(Received 21 November 2011; accepted 27 May 2012; published online 13 June 2012)

The magnetocaloric effect (MCE) at the antiferromagnetic (AF) to ferromagnetic (F) phase transition in Mn1.05Ni0.85Ge and CrO1.86F0.14, and the MCE at the F-AF transition in Tb3Co have been investigated. Mn1.05Ni0.85Ge and CrO1.86F0.14 are found to exhibit the inverse MCE whereas the MCE of Tb3Co is normal. For these compounds, the dependence of the transition temperature on the applied magnetic field has been studied. A thermodynamical analysis is presented of the sign of the magnetic-entropy change in these three compounds which are representatives of two different types of B-T diagrams. Other possible B-T diagrams are discussed and the analysis is extended to AF-F and F-AF phase transitions reported in literature. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4729122]

The magnetocaloric effect (MCE) is the change of temperature of a magnetic material, either heating or cooling, upon application of a magnetic field.1,2 Usually, a considerable MCE occurs at a magnetic phase transition. Because of its potential for very efficient and environment-friendly application in refrigeration, the MCE has been intensively investigated during the last decade and many materials such as Gd, Gd3(Si1-xGex) and MnFe(P1-xAsx), La(FeSi)13, have been reported to have a large concomitant MCE at the magnetic phase transition.3–6 At the transition from the ferromagnetic (F) to the paramagnetic (P) state, a so-called normal MCE is found which corresponds with a negative magnetic-entropy change ΔSM and positive adiabatic temperature change ΔTad when the magnetic field is increased. However, at the antiferromagnetic (AF) to F phase transition, either a normal or an inverse MCE (positive ΔSM and negative ΔTad with increasing magnetic field) can be found. The occurrence of these two possibilities is a challenging subject for study. In the present paper, the inverse MCE at the AF-F transition in the compounds Mn1.05Ni0.85Ge, and CrO1.86F0.14 and a normal MCE at the F-AF transition in Tb3Co is presented. The dependence of the transition temperature Tc on the applied magnetic field B has been investigated for these three compounds, a thermodynamic analysis of the obtained B-T phase diagrams is presented and is extended to other AF-F and F-AF phase transitions reported in literature.

At the AF-F phase transition, the free enthalpies GA and GF of the two phases in equilibrium should be equal, so that HA − TSF = HF − TSF, where H and S represent the enthalpy and entropy, respectively, of the AF and F phases. If the AF phase is stable at low temperatures, its enthalpy HA will be smaller than the enthalpy HF of the F phase. Via the −TSF term, the entropy SF of the high-temperature F phase, being evidently larger than SAF, drives the phase transition. In this case, ΔS = SF − SAF > 0. Following the same reasoning for the case that the F phase is stable at low temperature, it is found that ΔS = SF − SAF < 0.

If a magnetic field is applied, the free-enthalpy equilibrium condition becomes HA − TSF = HF − TSF − μB(T), where Bc is the critical field at which the phase transition occurs. From this, it follows that dBc/dT = −ΔS/μ with ΔS = SF − SAF and μ the magnetic moment of the F phase. It is seen that the sign of dBc/dT determines the sign of ΔS.

The experimental determination of the MCE includes the measurement of the magnetic-entropy change at the phase transition in B-T diagram by application of a magnetic field. Regarding the occurrence of the normal MCE (ΔS < 0) or the inverse MCE (ΔS > 0), above thermodynamic considerations show that the normal MCE will occur if the F phase is stable at low temperature. If AF is the stable low temperature phase, ΔS = SF − SAF > 0 and MCE is inverse. In total, as shown in Fig. 1, six schematic types of B-T phase diagrams can be considered. However, three of them can be anticipated to be unphysical. An applied magnetic field favors the F phase and the AF phase can be expected to become unstable at sufficiently large applied field. Therefore, the AF phase will only exist in the lower-field region in a B-T diagram and the diagrams of the types ④, ⑤, and ⑥ cannot be expected to exist. This also follows simply from above thermodynamic considerations. These diagrams do not obey the laws of thermodynamics because the sign of ΔS derived from the equilibrium condition of the two phases in the absence of an applied field does not agree with the sign of ΔS derived from dBc/dT. For sake of the discussion, we distinguish two regions in diagram ①, region ①a, where the AF to F transition occurs also without an applied magnetic field, and region ①b where the transition occurs in an applied magnetic field, also at zero temperature.
The compound MnNiGe has two different structures, one is the low-temperature orthorhombic TiNiSi-type AF phase with \( T_N = 346 \, \text{K} \), and the other is the high-temperature hexagonal Ni\(_2\)In-type phase with a paramagnetic Curie temperature of 277 K. With increasing temperature, MnNiGe undergoes phase transitions from orthorhombic AF to orthorhombic P, and from orthorhombic P to hexagonal P. To obtain hexagonal F MnNiGe, off-stoichiometric Mn\(_{1.9-x}\)Ni\(_{0.85}\)Ge alloys have been investigated by Zhang et al. The hexagonal F phase was obtained for \( x = 0.85 \) and 0.855. The temperatures of the magnetostructural transition from the AF TiNiSi-type structure to the F Ni\(_2\)In-type structure were found to be 140 K and 165 K, respectively, indicating that this temperature is very sensitive to the composition.

The temperature dependence of the critical field was derived from the magnetic isotherms at different temperatures.

FIG. 1. Schematic magnetic field vs temperature phase diagrams for phase transitions between AF and F. Six types of diagrams are shown, of which only the types 1, 2, and 3 do exist.

FIG. 2. (a) Temperature dependencies of the ZFC and FC magnetization of Mn\(_{1.05}\)Ni\(_{0.85}\)Ge in a magnetic field of 0.1 T, with \( T_c \) and \( T_F \) indicating the transition temperatures from AF to F and from F to P, respectively; (b) Temperature dependence of the ZFC magnetization of Mn\(_{1.05}\)Ni\(_{0.85}\)Ge at magnetic fields of 0.1, 0.5, 1, 2, and 5 T; (c) Dependence of the critical magnetic field of the AF to F transition on temperature.
followed by an AF to P transition at $T_N = 82$ K. The inset displays the shift of the F to AF transition with increasing magnetic field, as seen in the temperature dependence of the reduced magnetization. This finding is consistent with our previous results that were derived from magnetic isotherms measured at various temperatures around the transition. The temperature dependence of critical magnetic field is linear with a positive slope (Fig. 4(b) and, accordingly, the MCE at this F to AF transition is normal. The negative magnetic-entropy change, shown in Figs. 4(c), exhibits peaks at the temperatures $T_t$ and $T_N$, which are associated with the F to AF and the AF to P transition, respectively. The phase diagram of Tb$_3$Co is of type $\mathbb{2}$.

In Table I, the main characteristics of the three investigated systems have been summarized, together with a few more examples of the possible B-T phase diagrams that have been taken from literature and will be discussed below. The compound FeRh possesses an AF to F phase transition at 316 K, with a transition temperature $T_t$ that decreases to 292 K if the magnetic field is increased to 2.5 T. The B-T diagram is of type $\mathbb{1}$a and the MCE is inverse. The maximum magnetic-entropy change is 11.6 J/kg K for a magnetic-field change from 0 to 2.5 T. The compound Ni$_{1.95}$Mn$_{1.46}$In$_{0.59}$ has been reported to undergo a transition from AF martensite to F austenite at 285 K (Ref. 11) and it can be seen in Fig. 3 in Ref. 11 that the critical field

![Figure 3](image1.jpg)

![Figure 4](image2.jpg)

**TABLE I.** Parameters for materials exhibiting a normal or an inverse MCE at the AF to F transition: The type of magnetic transition and phase diagram, the sign of $\frac{dB_c}{dT}$, the magnetic-ordering temperature ($T_N$, $T_C$), the transition temperature $T_t$ in the absence of a magnetic field, and the type of MCE.

<table>
<thead>
<tr>
<th>Material</th>
<th>Transitions</th>
<th>Phase diagram</th>
<th>Sign of $\frac{dB_c}{dT}$</th>
<th>$T_C$ (K)</th>
<th>$T_N$ (K)</th>
<th>$T_t$ (K)</th>
<th>MCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$<em>{1.05}$Ni$</em>{0.85}$Ge$^a$</td>
<td>AF-F</td>
<td>$\mathbb{1}$a</td>
<td>Negative</td>
<td>205</td>
<td>...</td>
<td>100</td>
<td>Inverse</td>
</tr>
<tr>
<td>CrO$<em>{1.86}$F$</em>{0.14}$</td>
<td>AF-F</td>
<td>$\mathbb{1}$a</td>
<td>Negative</td>
<td>196</td>
<td>...</td>
<td>90</td>
<td>Inverse</td>
</tr>
<tr>
<td>FeRh$^{10}$</td>
<td>AF-F</td>
<td>$\mathbb{1}$a</td>
<td>Negative</td>
<td>650</td>
<td>...</td>
<td>316</td>
<td>Inverse</td>
</tr>
<tr>
<td>Ni$<em>{1.95}$Mn$</em>{1.46}$In$_{0.59}$</td>
<td>AF-F</td>
<td>$\mathbb{1}$a</td>
<td>Negative</td>
<td>316</td>
<td>...</td>
<td>285</td>
<td>Inverse</td>
</tr>
<tr>
<td>UNiAl$^{12}$</td>
<td>AF-F</td>
<td>$\mathbb{1}$b</td>
<td>Negative</td>
<td>...</td>
<td>19</td>
<td>...</td>
<td>Inverse</td>
</tr>
<tr>
<td>Tb$_3$Co$^{14}$</td>
<td>F-AF</td>
<td>$\mathbb{2}$</td>
<td>Positive</td>
<td>...</td>
<td>82</td>
<td>72</td>
<td>Normal</td>
</tr>
<tr>
<td>Gd$_3$Al$^{15,14}$</td>
<td>F-AF</td>
<td>$\mathbb{2}$</td>
<td>Positive</td>
<td>50</td>
<td>...</td>
<td>...</td>
<td>Normal</td>
</tr>
</tbody>
</table>

$^a$This work.
decreases with increasing temperature. Also, the B-T diagram of Ni$_{1.95}$Mn$_{1.46}$In$_{0.59}$ is of type $\Theta$a. The inverse MCE accompanying the AF to F transition in Ni$_{1.95}$Mn$_{1.46}$In$_{0.59}$ is reported in Ref. 11. The hexagonal ZrNiAl-type ternary compound UNiAl presents an example of an AF to F transition with a B-T diagram of type $\Theta$b. This compound is itinerant AF with $T_N = 19.3$ K. At low temperatures and at high magnetic-field values, larger than 11.35 T, the magnetic field induces an AF to F transition. The transition temperature $T_t$ decreases with increasing magnetic field and an inverse MCE has been reported, making UNiAl an excellent example of type $\Theta$b. As a last example, we mention the compound Gd$_2$Al which is AF with $T_N = 50$ K. At 4.5 K, a field-induced magnetic AF to F transition occurs at a critical field of 2.5 T. This field value increases a little with increasing temperature, which means $dB_c/dT$ is positive and that the MCE is normal. The latter is indeed obtained by applying the Maxwell equation to the magnetic isotherms in Refs. 13 and 14 and Gd$_2$Al can be considered as a nice example of a B-T diagram of type $\Theta$. In Table I, the types of magnetic transitions in the absence of a magnetic field, the type of phase diagram, the sign of the temperature dependence of critical magnetic field for the AF to F transition, the magnetic-ordering temperatures $T_N$ or $T_C$, and the type of MCE for the discussed compounds with F to AF or AF to F transition are summarized.

In conclusion, the temperature dependence of the critical magnetic field $B_c$ of the magnetic phase transition of Mn$_{1.05}$Ni$_{0.85}$Ge, CrO$_{1.86}$F$_{0.14}$ and Tb$_5$Co and the associated types of MCE have been investigated. In the former two compounds, the transition at $T_t$ is AF to F, with B-T diagram of type $\Theta$a, a negative $dB_c/dT$ and an inverse MCE; while the transition at $T_t$ in the latter one is F to AF of type $\Theta$, with a positive $dB_c/dT$ and a normal MCE. Other possible transition types and some related compounds collected from the literature are also discussed.

This work has been supported by the National Basic Research Program No. 2012CB619404, the Ministry of Science and Technology of China, and the National Natural Science Foundation of China under Grant No. 50831006.