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Normal or inverse magnetocaloric effects at the transition between antiferromagnetism and ferromagnetism

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The magnetocaloric effect (MCE) at the antiferromagnetic (AF) to ferromagnetic (F) phase transition in $Mn_{1.05}Ni_{0.85}Ge$ and $CrO_{1.86}F_{0.14}$, and the MCE at the F-AF transition in Tb_3Co have been investigated. $Mn_{1.05}Ni_{0.85}Ge$ and $CrO_{1.86}F_{0.14}$ are found to exhibit the inverse MCE whereas the MCE of Tb_3Co is normal. For these compounds, the dependence of the transition temperature on the applied magnetic field B 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. [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, $Gd_5(Si_{1-x}Ge_x)_4$ and $MnFe(P_{1-x}As_x)$, $La(FeSi)_{13}$ have been reported to have a large concomitant MCE at the magnetic phase transition.[2–6] 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 ΔS_M and positive adiabatic temperature change ΔT_{ad} when the magnetic field is increased. However, at the antiferromagnetic (AF) to F phase transition, either a normal or an inverse MCE (positive ΔS_M and negative ΔT_{ad} 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 $Mn_{1.05}Ni_{0.85}Ge$, and $CrO_{1.86}F_{0.14}$ and a normal MCE at the F-AF transition in Tb_3Co is presented. The dependence of the transition temperature T_t 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 G_{AF} and G_F of the two phases in equilibrium should be equal, so that $H_{AF} - TS_{AF} = H_F - TS_F$, 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 H_{AF} will be smaller than the enthalpy H_F of the F phase. Via the $-TS_F$ term, the entropy S_F of the high-temperature F phase, being evidently larger than S_{AF}, drives the phase transition. In this case, $\Delta S = S_F - S_{AF} > 0$. Following the same reasoning for the case that the F phase is stable at low temperature, it is found that $\Delta S = S_F - S_{AF} < 0$.

If a magnetic field is applied, the free-enthalpy equilibrium condition becomes $H_{AF} - TS_{AF} = H_F - TS_F - \mu B_c(T)$, where B_c is the critical field at which the phase transition occurs. From this, it follows that $dB_c/dT = -\Delta S/\mu$ with $\Delta S = S_F - S_{AF}$ and μ the magnetic moment of the F phase. It is seen that the sign of dB_c/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 ($\Delta S < 0$) or the inverse MCE ($\Delta S > 0$), 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, $\Delta S = S_F - S_{AF} > 0$ 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 dB_c/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.

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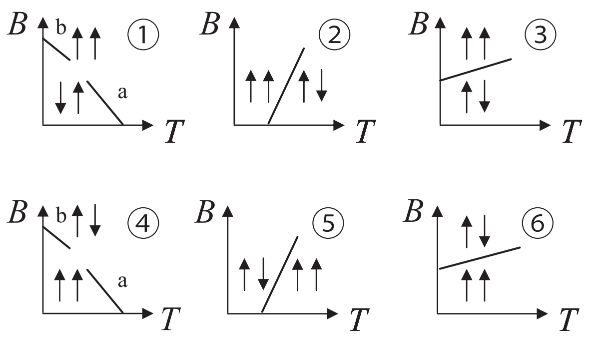

FIG. 1. Schematic magnetic field vs temperature phase diagrams for phase transitions between AF and F. Six types of diagrams are shown, of which only the types ①, ②, and ③ do exist.

Polycrystalline Tb_3Co and $Mn_{1.05}Ni_{0.85}Ge$ have been prepared by arc melting and subsequent annealing for obtaining homogeneity. Polycrystalline $CrO_{1.86}F_{0.14}$ was synthesized under a pressure of about 6 GPa at about 1200 °C. The x-ray diffraction patterns showed all prepared compounds to be single phase. The magnetic properties were measured in a superconducting quantum inference device magnetometer (MPMS-XL, Quantum Design). The transition temperatures were determined by determining the extremal value of the first-order derivative of the magnetization with respect to temperature. The temperature dependence of the critical field was derived from the magnetic isotherms at different temperatures.

The compound MnNiGe has two different structures, one is the low-temperature orthorhombic TiNiSi-type AF phase with $T_N = 346$ K, and the other the high-temperature hexagonal Ni_2In-type phase with a paramagnetic Curie temperature of 277 K.[7] 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 $Mn_{1.9-x}Ni_xGe$ alloys have been investigated by Zhang *et al.*[8] 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_2In-type structure were found to be 140 K and 165 K, respectively, indicating that this temperature is very sensitive to the composition. Figure 2(a) shows the temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization of $Mn_{1.05}Ni_{0.85}Ge$ in a magnetic field of 0.01 T. The divergence of the ZFC and FC curves indicates that the magnetostructural transition is first order. The Curie temperature T_C is 205 K and T_t of the AF to F transition is 100 K. Upon increasing magnetic field, the AF to F transition shifts to lower temperatures (Fig. 2(b)) and a linear relationship between the critical magnetic field and temperature is found (Fig. 2(c)). The slope is negative, so that the AF to F transition in $Mn_{1.05}Ni_{0.85}Ge$ is representative of type ①a. It follows that ΔS is positive, i.e., that the MCE is inverse. The positive magnetic-entropy change with a maximum value of 27 J kg^{-1} K^{-1} for a magnetic-field change from 0 to 5 T, as reported by Zhang *et al.*, confirms the occurrence of the inverse MCE.[8]

CrO_2 is a magnetic substance which is widely used in magnetic recording media. Compounds of the $CrO_{2-x}F_x$ series with $0.12 \le x \le 0.20$ have been synthesized under high-pressure and at high-temperature by Chamberland *et al.* and from the temperature dependence of the magnetization it has been deduced that these compounds undergo an AF to F phase transition.[9] The inset of Figure 3(a) shows the temperature dependence of the ZFC magnetization of $CrO_{1.86}F_{0.14}$ in a magnetic field of 0.05 T. The values of T_C and T_t are 186 K and 90 K, respectively. With increasing magnetic field, T_t shifts to lower temperatures, corresponding with a negative dB_c/dT (Fig. 3(b)), representing another example of a phase diagram of type ①a. In Fig. 3(a), the magnetic isotherms are shown from 45 to 110 K with temperature steps of 5 K. A magnetic isotherm at lower temperature crosses with one at higher temperature, which is ascribed to that the saturation magnetization of the (induced) F phase at higher temperature is smaller due to the temperature disorder. As shown in Fig. 3(c), the magnetic-entropy change evaluated by means of the Maxwell relation at a magnetic-field change from 0 to 1.5 T is inverse, which agrees with the negative sign of dB_c/dT.

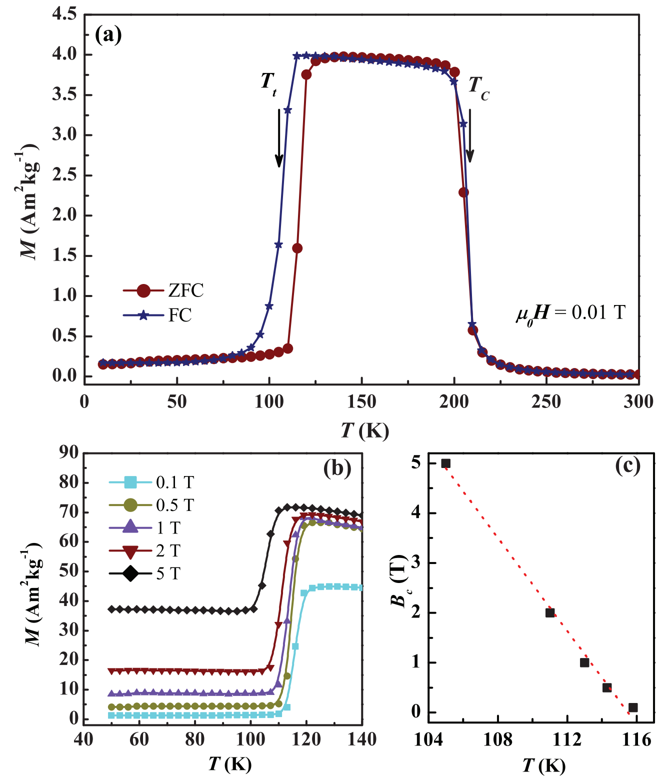

FIG. 2. (a) Temperature dependencies of the ZFC and FC magnetization of $Mn_{1.05}Ni_{0.85}Ge$ in a magnetic field of 0.1 T, with T_t and T_C indicating the transition temperatures from AF to F and from F to P, respectively; (b) Temperature dependence of the ZFC magnetization of $Mn_{1.05}Ni_{0.85}Ge$ 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.

Previously, we have suggested that Tb_3Co might be a promising magnetic-refrigeration material around the temperature window of liquid nitrogen.[4] Here, we focus on the MCE at lower magnetic-field changes. Figure 4(a) shows the temperature dependence of the ZFC and FC magnetization in a magnetic field of 0.05 T. The FC curve and the ZFC curve do not coincide because of the freezing of magnetic moments at low temperatures in the ZFC measurement. The compound undergoes an F to AF transition at $T_t = 72$ K,

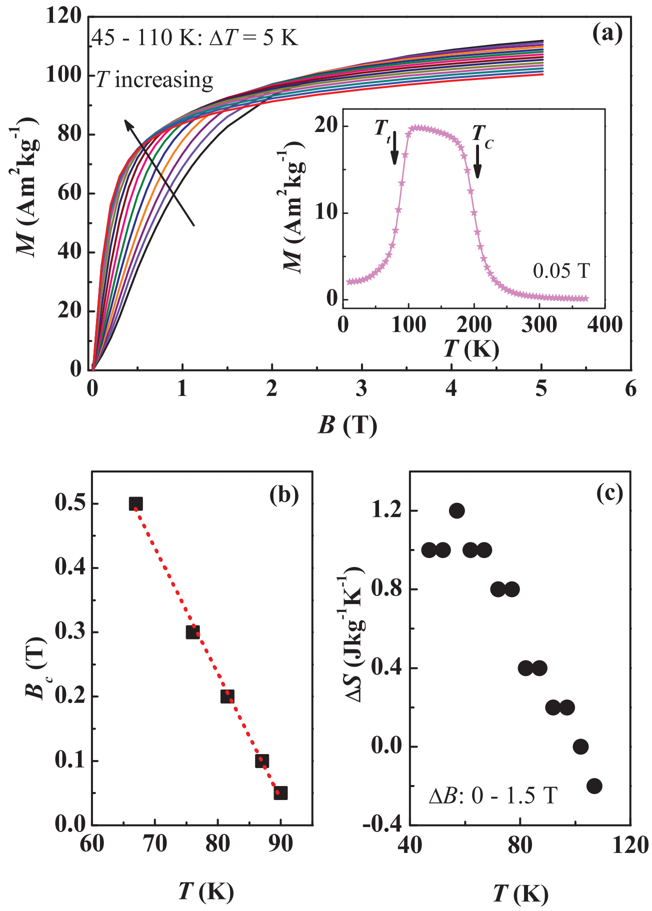

FIG. 3. (a) Magnetic isotherms of $CrO_{1.86}F_{0.14}$, measured from 45 to 110 K with temperature steps of 5 K. The inset shows the temperature dependencies of the ZFC and FC magnetization in a magnetic field of 0.05 T, with T_t and T_C indicating the transition temperatures from AF to FM and from FM to PM, respectively; (b) Temperature dependence of the critical magnetic field of the AF to FM transition. (c) Magnetic-entropy change at magnetic-field changes from 0 to 1.5 T.

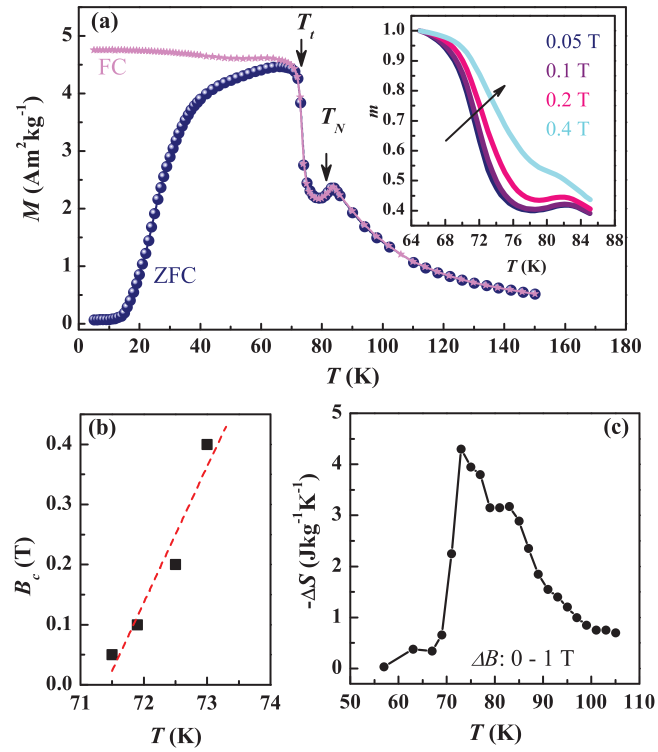

FIG. 4. (a) Temperature dependencies of the ZFC and FC magnetization of Tb_3Co in a magnetic field of 0.05 T, with T_t indicating the transition temperature from AF to F. The inset displays the temperature dependence of the ZFC reduced magnetization at different magnetic fields. (b) Temperature dependence of the critical magnetic field of the AF to F transition. (c) Magnetic-entropy change at magnetic-field changes from 0 to 1 T.

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_3Co is of type 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 ①a 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.[10] 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

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 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.

Material	Transitions	Phase diagram	Sign of dB_c/dT	T_C (K)	T_N (K)	T_t (K)	MCE
$Mn_{1.05}Ni_{0.85}Ge$[a]	AF-F	①a	Negative	205	…	100	Inverse
$CrO_{1.86}F_{0.14}$[a]	AF-F	①a	Negative	196	…	90	Inverse
FeRh[10]	AF-F	①a	Negative	650	…	316	Inverse
$Ni_{1.95}Mn_{1.46}In_{0.59}$[11]	AF-F	①a	Negative	316	…	285	Inverse
UNiAl[12]	AF-F	①b	Negative	…	19	…	Inverse
Tb_3Co[a,4]	F-AF	②	Positive	…	82	72	Normal
Gd_2Al[13,14]	F-AF	③	Positive	50	…	…	Normal

[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 ①a. 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 ①b. 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.[12] The transition temperature T_t decreases with increasing magnetic field and an inverse MCE has been reported, making UNiAl an excellent example of type ①b. As a last example, we mention the compound Gd_2Al 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.[13,14] 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_2Al can be considered as a nice example of a B-T diagram of type ③. 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_3Co 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 ①a, 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 ②, 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.

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