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Review

Magnetocaloric and barocaloric effects: Theoretical description and trends

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ABSTRACT

In this review paper we present a theoretical description of the magnetocaloric and barocaloric effects in metallic compounds. The theoretical formulation is separated in two categories namely, [1] systems whose magnetism is due to localized magnetic moments [2] systems whose magnetism is due to itinerant electrons. In both cases we perform systematic analysis of the magnetocaloric and barocaloric quantities in terms of the model parameters. Besides that, an application has been made to the real compounds $Tb_5Si_2Ge_2$ and $Mn(As_{0.7}Sb_{0.3})$.

Effets magnétocaloriques et barocaloriques: Description théorique et tendances

Mots clés : effet magnétocalorique ; effet barocalorique ; métal ; alliage ; modélisation thermodynamique

1. Introduction

The magnetocaloric effect (Brück, 2005; de Oliveira and von Ranke, 2010; Gschneidner Jr et al., 2005; Mañosa et al., 2013; Phan and Yu, 2007; Shen et al., 2009; Tishin, 2007; Tishin and Spichkin, 2003), which can be defined as the heating or cooling of magnetic materials upon magnetic field variation, is the basis of magnetic refrigeration, an environmental friendly technology which is supposed to replace the conventional one based on the compression and decompression of refrigerant fluids. Experimental data show that the compounds $Gd_5Si_2Ge_2$ (Pecharsky and Gschneidner, 1997), $Mn(As_{1-x}Sb_x$ (Gama et al.,

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Nomenclature

B	magnetic field
B	Brillouin function
$C_{B,P}$	specific heat at constant magnetic field and pressure
F^{4f}_{mag}	free energy of magnetic localized electrons
F^{d}_{mag}	free energy of magnetic itinerant electrons
g	Landé factor
g_{00}	local green function
J	total angular momentum
$\mathfrak{J}_0$	exchange integral interaction
$\mathfrak{J}_1$	magnetoelastic coupling parameter
k_B	Boltzmann constant
M	magnetization
N_m	number of magnetic ions per unit formula
N_i	number of total ions per unit formula
P	pressure
$\mathfrak{R}$	gas constant
S	total entropy
S_{el}	entropy of the non magnetic conduction electrons
S_{lat}	entropy of the crystalline lattice
S^{4f}_{mag}	entropy of the magnetic localized electrons
S^{d}_{mag}	entropy of the magnetic itinerant electrons
T	temperature
U^d	Coulomb interaction parameter
Z^{4f}_{mag}	partition function of the magnetic localized electrons
Z^{d}_{mag}	partition function of the magnetic itinerant electrons
ΔS_{iso}	isothermal entropy change for $\Delta B \neq 0$ and $\Delta P = 0$
ΔT_{ad}	adiabatic temperature change for $\Delta B \neq 0$ and $\Delta P = 0$
ΔS^{bar}_{iso}	isothermal entropy change for $\Delta B = 0$ and $\Delta P \neq 0$
ΔT^{bar}_{ad}	adiabatic temperature change for $\Delta B = 0$ and $\Delta P \neq 0$
ΔP	pressure variation
ΔB	magnetic field variation
Θ_D	Debye temperature
γ	Sommerfeld coefficient
$\gamma^{el}_0, \gamma^{el}_1, \gamma^{el}_2$	electronic magnetoelastic coupling parameters
γ_{ph}	Phonon magnetoelastic coupling parameter
μ_B	Bohr magneton
$\rho(\varepsilon)$	electronic density of states
ε_F	Fermi energy

2004; Wada and Tanabe, 2001; Wada et al., 2003, 2009), $MnFeP_{1-x}As_x$ (Tegus et al., 2002; Brück et al., 2003), $La(Fe_xSi_{1-x})_{13}$ (Fujita et al., 2003), which exhibit large values of the entropy change, are good candidates to be used as magnetic refrigerant in magnetic refrigerators.

In the last years, the magnetic barocaloric effect (de Oliveira, 2007, 2011, 2013; Mañosa et al., 2010, 2011, 2013; Müller et al., 1998; Santana et al., 2011b; Yuce et al., 2012), which is the heating or cooling of magnetic materials upon pressure variation, has drawn attention due to the fact that it can also be useful to improve the performance of magnetic refrigerators. Despite the possible application in magnetic refrigeration, the study of the magnetocaloric and barocaloric effects is also important from the point of view of fundamental physics.

The development of theoretical models to properly describe the magnetocaloric and barocaloric effects is important not only to explain the available experimental data but also to predict new and unexpected trends. In order to make an appropriate theoretical description of the magnetocaloric and barocaloric effects in metallic compounds, we have to consider the nature of the magnetic interactions. In this review paper we present a theoretical description of the magnetocaloric and barocaloric effects in two different types of compounds. In the first class are the rare earth compounds and their alloys, whose magnetism comes from localized magnetic moments. In the second class are the transition metals and their alloys whose magnetism comes from itinerant electrons.

The outline of this review paper is as follows. In Section 2, we present very briefly the basic concepts involved in the thermodynamics of the magnetocaloric and barocaloric effects. In Section 3, we present the theoretical models to describe the magnetocaloric and barocaloric effects taking into account the origin of the magnetism. In Section 3.1 we present the theoretical formulation for systems of localized magnetic moments. The theoretical formulation for systems of itinerant electrons is presented in Section 3.2. Finally, in Section 4, we present the conclusions and future challenges.

2. Thermodynamics

The magnetocaloric effect is usually characterized by a temperature change (ΔT_{ad}) in an adiabatic process and by an entropy change (ΔS_{iso}) in an isothermal process upon magnetic field variation. The quantity (ΔT_{ad}) can be measured directly or indirectly by using specific heat data or by a combination of specific heat and magnetization data. On the other hand, the quantity (ΔS_{iso}) can only be experimentally determined indirectly by using either specific heat or magnetization data. The magnetocaloric quantities ΔS_{iso} and ΔT_{ad} are determined by $\Delta S_{iso}(T, \Delta B, P) = S(T, B_2, P) - S(T, B_1, P)$ where $\Delta B = B_2 - B_1$ and by $\Delta T_{ad}(T, \Delta B, P) = T_2 - T_1$, upon the adiabatic condition $S(T, B_2, P) = S(T, B_1, P)$. These two magnetocaloric quantities can be better visualized in Fig. 1 where we show the total entropy at a fixed pressure as a function of temperature for two values of the applied magnetic field.

In order to get the mathematical relations for the magnetocaloric quantities, we consider the entropy as a function of temperature, magnetic field and pressure. Then we can write the total differential as

$$dS(T,B,P) = \left[\frac{\partial S(T,B,P)}{\partial T}\right]_{B,P} dT + \left[\frac{\partial S(T,B,P)}{\partial B}\right]_{T,P} dB + \left[\frac{\partial S(T,B,P)}{\partial P}\right]_{T,B} dP \qquad (1)$$