PRAMANA — journal of physics

Vol. 84, No. 6
June 2015
pp. 977–985

Magnetocaloric effect in rare-earth intermetallics: Recent trends

R NIRMALA[1,*], A V MOROZKIN[2] and S K MALIK[3]

[1]Department of Physics, Indian Institute of Technology Madras, Chennai 600 036, India
[2]Department of Chemistry, Moscow Lomonosov State University, Moscow, 119992, Russia
[3]Departamento de Física Teórica e Experimental, Universidade Federal do Rio Grande do Norte, Natal, 59082-970, Brazil
*Corresponding author. E-mail: nirmala@iitm.ac.in

DOI: 10.1007/s12043-015-1000-1; ***e*Publication:** 27 May 2015

Abstract. Magnetocaloric effect (MCE) is the change in isothermal magnetic entropy (ΔS_m) and adiabatic temperature (ΔT_{ad}) that accompany magnetic transitions in materials during the application or the removal of magnetic field under adiabatic conditions. The physics of MCE gets enriched by correlated spin-lattice degrees of freedom. This phenomenon has been actively investigated over the past few decades as it holds a promise for an alternate method of refrigeration/heat pumping. This has already resulted in several reviews on this topic. This paper focusses on some recent trends in this field and prospects of using rare-earth-based materials as active magnetic refrigerants over a broad temperature range that includes gas liquefaction and near-room temperature refrigeration/heating.

Keywords. Magnetocaloric effect; rare-earth intermetallics and alloys; magnetic properties.

PACS Nos 75.30.Sg; 71.20.Eh; 65.40 Gr

1. Introduction

Alternative cooling technology methods have gained increased attention in the last two decades, owing to the better awareness of the need to identify ecofriendly, cleaner and green technology. In this connection, magnetic refrigeration is proposed as one of the prospective methods. In addition to the ecofriendliness, improved Carnot efficiency, compaction and noise minimization are the other advantages associated with magnetic cooling [1,2]. For these reasons, extensive research is being carried out to identify suitable magnetic materials for their use as magnetic refrigerants in various temperature ranges. Magnetocaloric effect (MCE) is the change in isothermal magnetic entropy (ΔS_m) and adiabatic temperature (ΔT_{ad}) that accompany magnetic transitions in materials during the application or removal of magnetic field under adiabatic conditions. A paramagnet

shows large change in magnetization near absolute zero and hence is utilized for achieving ultralow temperatures, by a process that is well-known now as adiabatic demagnetization. Giant changes in isothermal magnetic entropy were noticed for the first time in a rare-earth intermetallic compound, namely, $Gd_5Si_2Ge_2$ around ~276 K (T_C), the temperature at which a simultaneous crystal structural and magnetic transition occurs [3]. This has indeed generated the ongoing quest for giant magnetocaloric materials by the condensed matter physicists. This long search has subsequently led to a huge number of reviews on this topic on various materials that span from rare-earth-based intermetallic compounds, intermetallic hydrides, manganite oxides, Ni–Mn–Sb-type shape memory alloys, Mn–Fe–P–Si-type all-transition metal compounds and most recently to ferroic materials [4–16]. In this report, an effort has been made to update this list by adding some rare-earth intermetallic compounds of recent interest.

2. Measurement of magnetocaloric effect

Magnetocaloric effect can be measured in terms of (i) isothermal magnetic entropy change and (ii) adiabatic temperature change. One more associated measure is the figure-of-merit parameter, namely, the relative cooling power (RCP) [17–20].

2.1 *MCE from magnetization data*

The change in isothermal magnetic entropy is calculated by using magnetization (M) vs. field (H) data measured at different temperatures near the magnetic transition temperature (T_C/T_N, of a ferromagnet/ferrimagnet/antiferromagnet). The ΔS_m is often computed by numerically integrating the thermodynamic Maxwell relation, $(\partial S/\partial H)_T = (\partial M/\partial T)_H$,

$$\Delta S_m(T, H) = S_m(T, H) - S_m(T, 0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H. \tag{1}$$

Making a numerical approximation to eq. (1), ΔS_m can be calculated from the measurement of isothermal magnetization performed at small, discrete magnetic field intervals at different temperatures near T_C for a ferromagnet, using the formula

$$|\Delta S_m| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H, \tag{2}$$

where M_i and M_{i+1} are the values of magnetization at temperatures T_i and T_{i+1}, respectively.

2.2 *MCE from heat capacity data*

The change in isothermal magnetic entropy can also be computed from heat capacity (C) vs. temperature data measured in zero magnetic field and in applied magnetic field using the following relation [eq. (3)]:

$$\Delta S_m(T, H) = \int_0^T \frac{C(T, H) - C(T, 0)}{T} \mathrm{d}T, \tag{3}$$

where $C(T, 0)$ and $C(T, H)$ are the heat capacities of the sample measured at temperature T in zero magnetic field and in an applied field H.

With the help of temperature-dependent heat capacity information in various applied fields, one can also calculate the change in adiabatic temperature, using eq. (4), after extracting the entropy ($S(T)$) from the heat capacity.

$$\Delta T_{\mathrm{ad}}(T)_{\Delta H} \cong [T(S)H_{\mathrm{f}} - T(S)H_{\mathrm{i}}]_S. \tag{4}$$

Here, H_{i} and H_{f} are the values of initial and final magnetic field. The uncertainty in each of these measurements is discussed in detail in refs [18,20].

2.3 *Relative cooling power*

Relative cooling power of a refrigerator is defined as the amount of heat transfer between the hot and the cold reservoir during the complete refrigeration cycle and is used as a key parameter to quantify the efficiency of the refrigerator. RCP is calculated as the area under the ΔS_{m} vs. T curve [1] using the following formula:

$$\mathrm{RCP} = \Delta S_{\mathrm{m}}^{\mathrm{max}} \times \Delta T_{\mathrm{FWHM}}, \tag{5}$$

where $\Delta T_{\mathrm{FWHM}} = T_{\mathrm{hot}} - T_{\mathrm{cold}}$. Here T_{hot} and T_{cold} are the temperatures below and above T_{C}, at 50% of the maximum magnetic entropy change, $\Delta S_{\mathrm{m}}^{\mathrm{max}}$, respectively.

2.4 *MCE from direct methods*

First-order magnetic and magnetostructural transitions are interesting as they result in giant magnetocaloric effect with additional functionality [21] but bring more uncertainty in the computation of MCE by the above techniques. Hence direct measurement of the change in adiabatic temperature is favoured [19,22–24]. The direct measurement gives only the measure of change in adiabatic temperature but can involve more experimental time for achieving adiabatic conditions and also precise measurement of temperature at various spots on the sample. Pulsed fields have also been used in the direct measurements which, however, bring more inaccuracy [19].

3. Magnetocaloric effect in rare-earth intermetallics

Although MCE is an intrinsic property of all magnetic materials, rare-earth metals, their alloys and compounds are expected to show interesting, huge, field-tunable magnetic entropy changes because of the intrinsically large molar magnetic entropy values associated with tripositive rare-earth ions. In addition, value of magnetic moment corresponding to the 4*f* electrons of rare earths is larger than those of a typical 3*d* electron system by a factor of 2 or more.

3.1 *Topical materials showing first-order transition*

After more than two decades of activity in this field, the elemental Gd continues to be considered as a prototype material for near-room temperature magnetic refrigeration applications because Gd orders ferromagnetically around 293 K and, most importantly, the isotropy of Gd^{3+} ion minimizes crystal field effects and anisotropy contributions to

Table 1. Values of isothermal magnetic entropy change for 2 T field change and the corresponding relative cooling power of typical magnetocaloric materials for near-room temperature magnetic cooling applications (data from ref. [3]).

Compound	T_C (K)	$-\Delta S_m^{max}$ (J/kg-K)	RCP (J/kg)
Gd	294	4.98	230
$Gd_5Si_2Ge_2$	276	14	108

the magnetism. The giant magnetocaloric material $Gd_5Si_2Ge_2$ and the related $Gd_5(Si, Ge)_4$ phases are considered the next best candidates (table 1) [2,3,25]. The variation in Si:Ge ratio in these compounds yields a wide tunability in magnetic transition temperature (from ∼20 K to ∼280 K) retaining the giant MCE through most of the phase diagram [26].

Cubic Laves phase RCo_2 (where R = Dy, Ho and Er) intermetallic compounds also show large magnetocaloric effect near their first-order ferrimagnetic transition and these have attracted equal attention because most of these compounds also exhibit first-order itinerant metamagnetic transition and associated large MCE [27]. A wide range of substitutions at the transition metal site and the rare-earth metal site has been made and there are a number of publications and review articles on the magnetocaloric properties of Laves phases [28–31].

3.2 *Materials with broad magnetic entropy change*

In general, broad $\Delta S_m(T)$ and hence large value of RCP is realized in a material that undergoes a second-order magnetic transition. These materials are free from thermal and field hysteresis losses that render better energy efficiency. In this connection, Gd

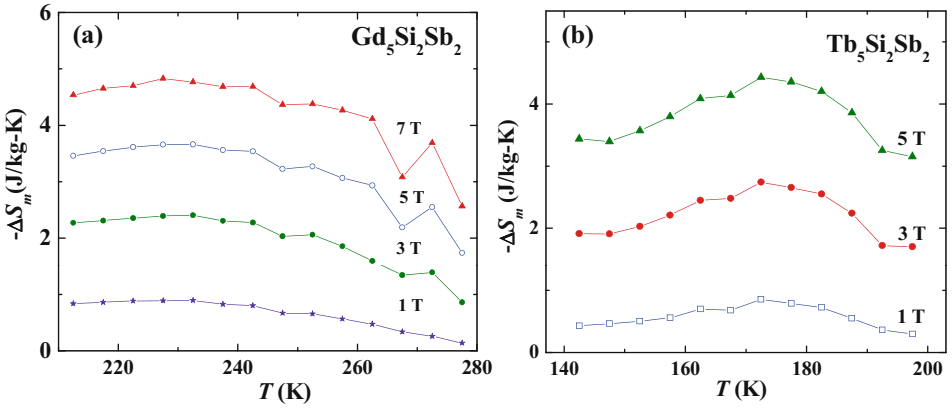

Figure 1. Change in isothermal magnetic entropy vs. temperature for (**a**) $Gd_5Si_2Sb_2$ and (**b**) $Tb_5Si_2Sb_2$ compounds near T_C for various magnetic field changes (from refs [32,33]).

and Gd-based compounds that do not show structural transition show superior magnetothermal properties. The compounds such as $Gd_5Si_2Sb_2$ (orthorhombic, Sm_5Ge_4-type) and $Tb_5Si_2Sb_2$ (orthorhombic, $Tm_5Si_2Sb_2$-type) exhibit table-like magnetocaloric effect where maximum in ΔS_m is spread over a wide temperature range near their magnetic transition temperatures (T_C ~266 K and ~181 K for the $Gd_5Si_2Sb_2$ and $Tb_5Si_2Sb_2$ samples and the useful temperature ranges are from ~215–260 K and ~150–195 K respectively) and this is useful in Ericson-cycle magnetic refrigeration application (figures 1a and 1b) [32,33].

3.3 *Materials with multiple magnetic transitions*

Very often, rare-earth transition metal compounds have more than one magnetic sublattices and these can order at different temperatures. If the magnetic transition temperatures are substantially closely spaced, the isothermal magnetic entropy may show a peak at each of these temperatures. For higher applied field changes, the peaks may shift and merge to form one broader peak in the ΔS_m vs. T curve. This leads to enhanced RCP values and larger working temperature spans. For example, the cubic Laves phase compound HoCoNi (space group Fd-3m) orders ferromagnetically at ~42 K and shows a spin-reorientation-like transition at ~11 K (T_{SR}) [30]. The peaks near T_C and T_{SR} in the ΔS_m vs. T data merge to give a broad maximum (figure 2) and hence a good number for relative cooling power and a wide working temperature range of about 10–65 K [34]. Similarly, large MCE and broad $\Delta S_m(T)$ behaviour are reported in the ErGa intermetallic compound wherein the close proximity of the two transitions leads to large RCP [35].

3.4 *Materials showing metamagnetic transition*

Metamagnetic or field-induced magnetic transitions occur in rare-earth intermetallic compounds and these have various origins. For example, some may be due to an itinerant

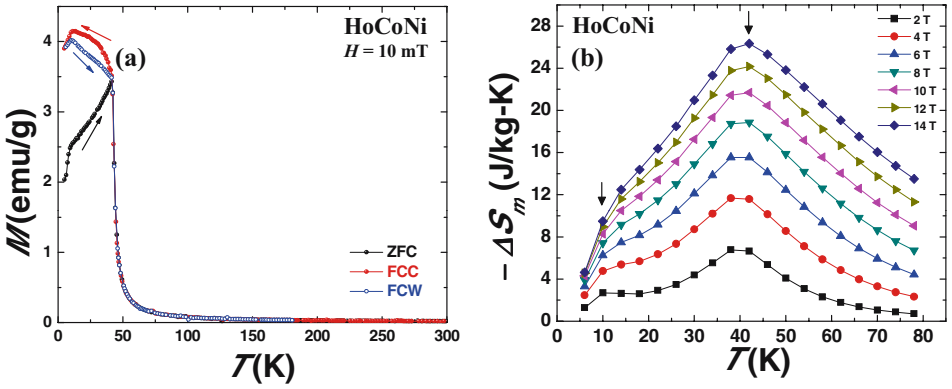

Figure 2. (**a**) Magnetization vs. temperature of HoCoNi compound in 10 mT field measured in zero-field-cooled (ZFC) and field-cooled cooling (FCC) and warming (FCW) cycles and (**b**) isothermal magnetic entropy change vs. temperature of HoCoNi for various magnetic field changes (ref. [34]).

electron subsystem in addition to the rare earth as in Laves phase compounds [28,36,37] or due to a change of magnetic structure within the ordered state. Metamagnetism can also result from a field-induced change of crystal structure as in Gd_5Ge_4 [38]. Sometimes, metamagnetism may result from strong anisotropy. Also intermetallic compounds with magnetic ions in different sublattices could lead to complex metamagnetic steps in M vs. H data. The large changes in magnetization values around the critical field reflect in the temperature dependence of ΔS_m and ΔT_{ad}. For example, the $Dy_5Si_2Ge_2$, DySi and RTiGe compounds show interesting metamagnetic behaviour in their magnetically ordered state [39–41]. In particular, the $Dy_5Si_2Ge_2$ compound (orthorhombic, Sm_5Ge_4-type) orders antiferromagnetically with $T_N \sim 56$ K and undergoes metamagnetic transition at temperatures below 40 K. This leads to enhanced magnetocaloric effect with an additional peak feature below T_N for field changes above 2 T (figure 3). This large MCE is spanned over 12–56 K. While first-order metamagnetic transitions may occur with

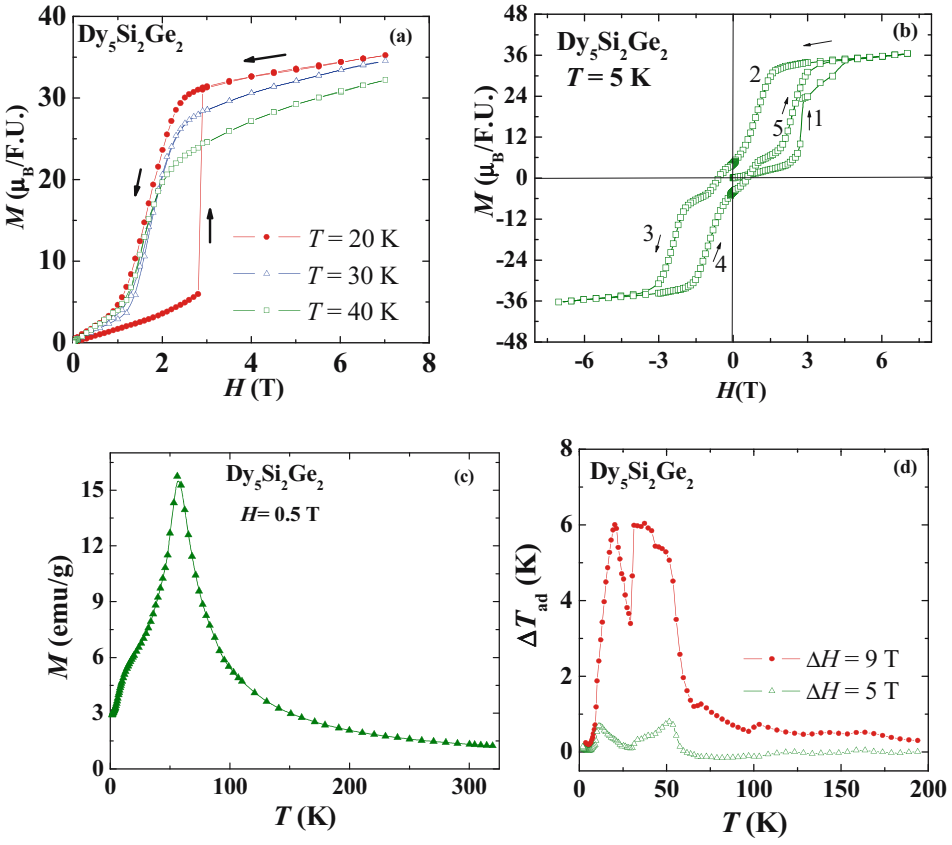

Figure 3. (**a,b**) Magnetization vs. field for $Dy_5Si_2Ge_2$ compound at selected temperatures (the numbers and arrows in the figure indicate the field cycle path), (**c**) magnetization vs. temperature for $Dy_5Si_2Ge_2$ in 0.5 T field and (**d**) change in adiabatic temperature vs. temperature for $Dy_5Si_2Ge_2$ (ref. [39]).

Table 2. Magnetic and magnetocaloric properties of a few selected Fe_2P-type R_6TX_2 (R = Ho, T = Fe, Co and Ru and X = Bi, Te) compounds [43].

Compound	T_C (K)	$-\Delta S_m^{max}$ (J/kg-K) for 5 T field change
Ho_6CoBi_2	68	8.2
Ho_6RuBi_2	32	8.5
Ho_6FeTe_2	27	12.9

field hysteresis, there are materials showing a second-order metamagnetic transition and these do not show any hysteresis. Thus, metamagnets offer additional field-tuned large magnetization.

3.5 *Materials with competing anisotropy*

Apart from the conventional rare-earth intermetallic alloys and compounds based on heavy rare earths, recently, transition metal-based Fe_2P-type compounds of the type $(Mn, Fe)_2(P, As)$ have gained interest [14,15]. In this connection, novel R_6TX_2 (R = heavy rare earth, T = Co, Ni and Mn, X = Si, Ge, Sb) compounds of the Fe_2P-type have been investigated for their magnetic and magnetocaloric properties [42,43] (table 2). In these compounds, magnetocrystalline anisotropy could play a vital role in addition to the magnetic exchange, leading to multiple/successive magnetic transitions in the magnetically ordered state which gives the possibility of field tunability and merger of maxima in $\Delta S_m(T)$ as discussed in §3.3. Studies on a single crystal, antiferromagnetic DySb compound reveal a giant but highly anisotropic magnetocaloric effect suggesting the possibility of using magnetic orientation to enhance the change in magnetic entropy [44]. Similarly, the observation of unusual and large MCE in the Dy_2Al compound is attributed to competing large magnetocrystalline anisotropy [45]. Also, recently R_3Co (R = heavy rare earth including Tm) compounds of Fe_3C-type orthorhombic structure have been well characterized for their interesting MCE behaviour that is expected to originate from the influence of the low symmetry crystalline electric field [46,47]. While the Er_3Co compound shows large reversible MCE centred at its ferromagnetic ordering temperature of 14 K, Tm_3Co compound undergoes a ferromagnetic order at $\sim$6.5 K that is closely spaced to the antiferromagnetic ordering that happens at $\sim$4.5 K. Interestingly, Tm_3Co does not show any thermal or magnetic hysteresis loss near the first-order metamagnetic transition making it a prospective material for low-temperature magnetic refrigeration applications.

4. Summary and conclusions

Thus, the rare-earth intermetallic compounds offer ample scope for finding suitable magnetic refrigerants in various working temperature ranges, in addition to the underlying complex physics. Although the cost of rare-earth metals is of concern, as one has found a way around them to make permanent magnets, their use in magnetic refrigeration applications need not be too far from reality.

Acknowledgements

RN thanks DAE-BRNS and DST, India for project support under YSRA and fast track schemes at different stages of this work. RN and AVM thank DST-RFBR for a collaborative project. SKM thanks CAPES, Brazil for the award of a fellowship during the course of this work. The authors also thank all their collaborators for their continuous support.

References

[1] S B Roy, *Handbook of magnetic materials* edited by K H J Buschow (North-Holland Publishers, The Netherlands, 2014) Vol. 22, Chap. 2
[2] V K Pecharsky and K A Gschneidner Jr, *Int. J. Refrigeration* **29**, 1239 (2006)
[3] V K Pecharsky and K A Gschneidner Jr, *Phys. Rev. Lett.* **78**, 4494 (1997)
[4] A M Tishin, *J. Magn. Magn. Mater.* **316**, 351 (2007)
[5] E Brück, *J. Phys. D* **38**, R381 (2005)
[6] K A Gschneidner Jr, V K Pecharsky and A O Tsokol, *Rep. Prog. Phys.* **68**, 1479 (2005)
[7] A M Tishin and Y I Spichkin, in: *The magnetocaloric effect and its applications* (IOP Publishing, Bristol, 2003)
[8] K A Gschneidner Jr and V K Pecharsky, Intermetallic compounds, in: *Principles and practice* edited by J H Westbrook and R L Fleischer (John Wiley & Sons Ltd, 2002) Vol. 3
[9] K A Gschneidner Jr and V K Pecharsky, *Annu. Rev. Mater. Sci.* **30**, 387 (2000)
[10] V K Pecharsky and K A Gschneidner Jr, *J. Magn. Magn. Mater.* **200**, 44 (1999)
[11] M-H Phan and S-C Yu, *J. Magn. Magn. Mater.* **308**, 325 (2007)
[12] J Liu, T Gottschall, K P Skokov, J D Moore and O Gutfleisch, *Nat. Mater.* **11**, 620 (2012)
[13] T Krenke, E Duman, M Acet, E F Wassermann, X Moya, L Mañosa and A Planes, *Nat. Mater.* **4**, 450 (2005)
[14] N H Dung, Z Q Ou, L Caron, L Zhang, D T Cam, G A Thanh, R A de Wijs, K H de Groot, J Buschow and E Brück, *Adv. Energy Mater.* **1**, 1215 (2011)
[15] O Tegus, E Brück, K H J Buschow and F R de Boer, *Nature (London)* **415**, 150 (2002)
[16] X Moya, S Kar-Narayan and N D Mathur, *Nat. Mater.* **13**, 439 (2014)
[17] A M Tishin, K A Gschneidner Jr and V K Pecharsky, *Phys. Rev. B* **59**, 503 (1999)
[18] V K Pecharsky and K A Gschneidner Jr, *J. Appl. Phys.* **86**, 565 (1999)
[19] A M Tishin, *Handbook of magnetic materials* edited by K H J Buschow, 1999) Chapter 4
[20] M Foldeaki, W Schnelle, E Gmelin, P Benard, B Koszegi, A Giguere, R Chahine and T K Bose, *J. Appl. Phys.* **81**, 309 (1997)
[21] P Chaddah, *Pramana – J. Phys.* **67**, 113 (2006) and references therein
[22] A Giguère, M Foldeaki, B Ravi Gopal, R Chahine, T K Bose, A Frydman and J A Barclay, *Phys. Rev. Lett.* **83**, 2262 (1999)
[23] E Palacios, G F Wang, R Burriel, V Provenzano and R D Shull, *J. Phys.: Conf. Ser.* **200**, 092011 (2010)
[24] V K Pecharsky and K A Gschneidner Jr, *J. Appl. Phys.* **86**, 6315 (1999)
[25] K A Gschneidner Jr, *Acta Mater.* **57**, 18 (2009)
[26] V K Pecharsky and K A Gschneidner Jr, *Appl. Phys. Lett.* **70**, 3299 (1997)
[27] N H Duc, D T Kim Anh and P E Brommer, *Physica B* **319**, 1 (2002)
[28] N H Duc and P E Brommer, *Handbook of magnetic materials* edited by K H J Buschow (North-Holland, Amsterdam, 1999) Vol. 12, Chap. 3
[29] Niraj K Singh, K G Suresh, A K Nigam, S K Malik, A A Coelho and S Gama, *J. Magn. Magn. Mater.* **317**, 68 (2007) and references therein
[30] Rajib Mondal, R Nirmala, J Arout Chelvane and A K Nigam, *J. Appl. Phys.* **113**, 17A930 (2013)

[31] Rajib Mondal, R Nirmala, J Arout Chelvane and A K Nigam, *Physica B* **448**, 9 (2014)
[32] R Nirmala, A V Morozkin and S K Malik, *Europhys. Lett.* **72**, 652 (2005)
[33] R Nirmala, A K Nigam and S K Malik, *Solid-State Commun.* **146**, 121 (2008)
[34] Rajib Mondal, R Nirmala, J Arout Chelvane, A K Nigam and S K Malik, unpublished
[35] J Chen, B G Shen, Q Y Dong, F X Hu and J R Sun, *Appl. Phys. Lett.* **95**, 132504 (2009)
[36] J Lyubina, K Nenkov, L Schultz and O Gutfleisch, *Phys. Rev. Lett.* **101**, 177203 (2008)
[37] S B Roy, G K Perkins, M K Chattopadhyay, A K Nigam, K J S Sokhey, P Chaddah, A D Caplin and L F Cohen, *Phys. Rev. Lett.* **92**, 147203 (2004)
[38] M K Chattopadhyay, M A Manekar, A O Pecharsky, V K Pecharsky, K A Gschneidner, J Moore, G K Perkins, Y V Bugoslavsky, S B Roy, P Chaddah and L F Cohen, *Phys. Rev. B* **70**, 214421 (2004)
[39] R Nirmala, A V Morozkin and S K Malik, *Phys. Rev. B* **75**, 094419 (2007)
[40] R Nirmala, A V Morozkin, D Buddhikot and A K Nigam, *J. Magn. Magn. Mater.* **320**, 1184 (2008)
[41] R Nirmala and S K Malik, *Europhys. Lett.* **80**, 27001 (2007)
[42] A V Morozkin, Y. Mozharivskyj, V Svitlyk, R Nirmala, O Isnard, P Manfrinetti, A Provino and C Ritter, *J. Solid State Chem.* **183**, 1314 (2010)
[43] S K Malik, A V Morozkin and R Nirmala, unpublished
[44] D X Li, S Nimori and T Shikama, *Solid-State Commun.* **150**, 1865 (2010)
[45] A Bhattacharyya, S Giri and S Majumdar, *J. Phys.: Condens. Matter* **22**, 316003 (2010)
[46] Pramod Kumar, N K Singh, A K Nayak, A Halder, K G Suresh and A K Nigam, *J. Appl. Phys.* **107**, 09A932 (2010)
[47] Z-J Mo, J Shen, L-Q Yan, J-F. Wu, C-C Tang and B G Shen, *J. Alloy Compd.* **572**, 1 (2013)