Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Magnetism and Magnetic Materials 290–291 (2005) 8–13
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Magnetocaloric effects in $MnFeP_{1-x}As_x$-based compounds

E. Brück[a,*], M. Ilyn[b], A.M. Tishin[b], O. Tegus[a]

[a]Van der Waals-Zeeman Instituut, Universiteit van Amsterdam, 1018XE Amsterdam, The Netherlands
[b]Department of Physics, Moscow State University, Moscow 119899, Russian Federation

Available online 2 December 2004

Abstract

Here we present the results of an investigation of some magnetic and thermal properties of the compounds $MnFeP_{0.45}As_{0.55}$, $MnFeP_{0.47}As_{0.53}$, and $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$ which can be regarded as possible magnetic refrigerants for room temperature applications. Magnetization measurements are performed in the temperature range 250–330 K, in magnetic fields up to 5 T. The coexistence of the magnetic and structural first-order phase transitions is revealed in all three samples, suggesting its key role in the large values observed for the magnetocaloric effect. The adiabatic temperature change measured directly was up to 4.0, 3.4, and 4.2 K for a magnetic field change of 1.45 T.

PACS: 71.20.Be; 75.30.Kz; 75.30.Sg

Keywords: Transition metal compounds; Phase transition first order; Magnetocaloric effect

1. Introduction

Modern society relies very much on readily available cooling. The world market for small units is currently about 140 million units per year. The vapor-compression cycle has dominated the refrigeration market to date because of its advantages: high efficiency, low toxicity, low cost, and simple mechanical embodiments. As much as 90% of the world's heat pumping power, i.e. refrigeration, water chilling, air conditioning, various industrial heating and cooling processes among others, is based on the vapor-compression-cycle principle. Alternatives for this technology are needed due to environmental concerns (ozone depletion, greenhouse effects, flammability). The ideal cooling machine would be a compact, solid-state, silent, energy-efficient heat pump, which does not require maintenance. Magnetic refrigeration based on the MCE may be the solution.

In recent years, environmental aspects have become an increasingly important issue in the design and development of refrigeration systems. Especially in vapor-compression systems, the banning of CFCs and HCFCs because of their environmental disadvantages has made way for other refrigeration technologies, which until now have been largely ignored by the refrigeration market. As environmental concerns grow, alternative technologies, that use either inert gases or no fluid at all, become attractive solutions of the environment problem. A significant part of the refrigeration-industry R&D expenditures is now worldwide oriented towards the development of such alternative technologies to replace vapor-compression systems in a mid- to long-term perspective.

Refrigerators should consume as low amounts of energy as possible. Magnetic refrigeration has intrinsically a high energy-efficiency, because it involves the alteration of entropy in quantum-mechanical systems

*Corresponding author. Tel.: +31 20 525 5640; fax: +31 20 525 5788.
E-mail address: bruck@science.uva.nl (E. Brück).

0304-8853/$ - see front matter
doi:10.1016/j.jmmm.2004.11.152

where no friction exists as demonstrated in experiments that aim at ultra-low temperatures. Magnetic refrigeration research strongly revived recently due to new developments both on the machine design and materials properties. The world's first room-temperature, permanent-magnet-based, magnetic refrigerator was built in America and, in Japan, Chubu and Toshiba released their high-efficiency cooler also based on permanent magnets [1]. Magnetic refrigeration has three prominent advantages compared to compressor-based refrigeration. First there are no harmful gasses involved, second it may be built more compactly as the working material is a solid, and third magnetic refrigerators generate much less noise.

Following the discovery of a sub-room-temperature giant MCE in the ternary compound $Gd_5(Ge_{1-x}Si_x)_4$ ($0.2 \leqslant x \leqslant 0.5$) by Pecharsky and Gschneidner [2], there is a strongly increased interest from both fundamental and practical points of view to study the MCE in Gd-based materials [3–5]. The common feature of these compounds is that they undergo a first-order structural and magnetic phase transition, which leads to a giant magnetic-field-induced entropy change, across their ordering temperature. Many other materials have been studied with respect to their magnetocaloric properties. Here, we will mention only a few of them; for a recent review of various aspects of magnetic refrigeration, see the book of Tishin and Spichkin [6]. The perovskite oxides $La_{1-x}Ca_xMnO_3$ show considerable MCE values [7,8]. Transition metal-pnictides such as $MnP_{1-x}As_x$ [9] and chalcogenides like Cr_3Te_4 [10] have been studied. The nearly equiatomic alloy FeRh undergoes a magnetic and structural order-order transformation and exhibits a giant MCE between 296 and 316 K but its MCE is irreversible and disappears after the first application of the magnetic field [11,12]. The Heusler alloys Ni–Mn–Ga show large magnetic-entropy changes that are due to an abrupt change of the magnetization near the martensite-to-austenite structural transition [13,14]. The compound $La(Fe,Co)_{11.83}Al_{1.17}$ with a very low rare-earth content also shows a considerable magnetocaloric effect near room temperature [15]. The MCEs in most transition-metal-based alloys are lower than in lanthanide-based alloys for the same temperature range, especially if one takes into account the fact that ΔT also depends on the specific heat of the compound [16]. This makes them unlikely candidates for use as magnetic refrigerant materials below room temperature. However, above room temperature there exist only a very limited number of rare-earth compounds exhibiting magnetic ordering, a prerequisite for showing large magnetocaloric effects. Fortunately, there exist many Mn compounds, such as MnAs [17], which display a variety of structural and magnetic phase transitions in the relevant temperature range. For a working material in a magnetic refrigerator, it is however essential that the phase transition is also reversible, which implies that field- or temperature-induced transitions should show little or no hysteresis.

Recently, we discovered a new class of magnetic refrigerant materials for room-temperature applications, described in an article published in Nature [18]. The new materials are manganese–iron–phosphorus-arsenic (MnFe(P,As)) and related compounds [19,20]. Also, interstitial modifications of the compounds $La(Fe,Si)_{13}$ and $La(Fe,Al)_{13}$ with hydrogen, carbon, and nitrogen [20–26] have attracted much attention. These new materials have important advantages over existing magnetic coolants: they exhibit a large magnetocaloric effect (MCE), larger than that of Gd metal, which is used in the refrigerators mentioned above, and the operating temperature can be tuned from below 200 to about 400 K by adjusting the chemical composition or the content of interstitial atoms.

Hysteresis effects and the difficulty of measuring specific heat at a first-order phase transition complicate the comparison of different magnetocaloric materials. Direct measurements of the adiabatic temperature change are an experimental technique that serves a way to get an immediate value of the MCE, omitting the intermediate calculation. The direct measurements of the MCE of $Gd_5(Ge,Si)_4$ and $La(Fe,Si)_{13}$ were performed earlier [27,28]. Here we report on direct measurements of the MCE in MnFe(P,As) compounds.

2. Experimental

Polycrystalline samples of $MnFeP_{0.45}As_{0.55}$, $MnFeP_{0.47}As_{0.53}$, and $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$ were prepared by ball-milling and solid-state reaction method as previously reported [18]. The magnetization measurements were carried out in a SQUID magnetometer Quantum Design MPMS5S in the temperature range 5–400 K and magnetic fields up to 5 T. The direct measurement of the magnetocaloric effect was carried out under adiabatic conditions with a continuous registration of the temperature change upon a fast increase of the applied magnetic field. The rate of the field change was up to $0.4\,T\,s^{-1}$. The accuracy of the measurements was about 5–20% depending on the temperature interval. A comprehensive description of this experimental technique is available in the review [6].

3. Results

The temperature dependence of the magnetization of the compounds $MnFeP_{0.45}As_{0.55}$, $MnFeP_{0.47}As_{0.53}$, and $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$ measured in a field of 10 mT is presented in Fig. 1. The abrupt change of the magnetization together with the temperature hysteresis

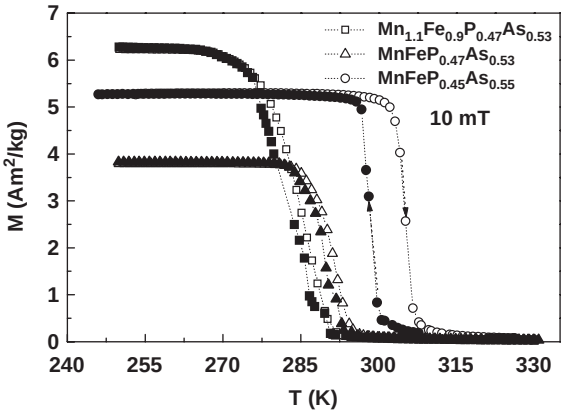

Fig. 1. Temperature dependence of the magnetization for $MnFeP_{0.45}As_{0.55}$, $MnFeP_{0.47}As_{0.53}$, and $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$ measured with increasing and decreasing temperature in a field of 10 mT.

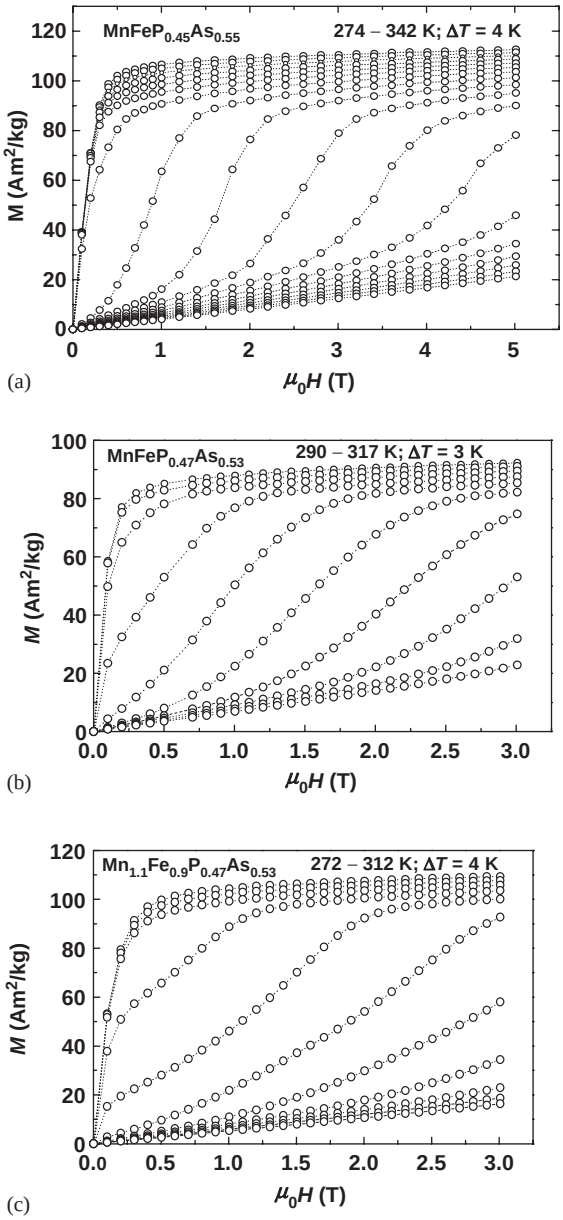

Fig. 2. (a) Magnetization isotherms of $MnFeP_{0.45}As_{0.55}$, (b) $MnFeP_{0.47}As_{0.53}$, and (c) $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$ on field increase.

reveals the first-order character of the phase transition. Additional magnetic states other than the ferromagnetic and the paramagnetic ones are not observed. The thermal hysteresis is more pronounced for the sample with higher contents of As. From the measurements performed with increasing temperature, we determine the Curie temperatures as 306, 293, and 289 K for $MnFeP_{0.45}As_{0.55}$, $MnFeP_{0.47}As_{0.53}$, and $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$, respectively. The isothermal magnetization curves collected at a certain temperature in an external magnetic field are shown in Figs. 2(a), (b), and (c) for $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$, $MnFeP_{0.47}As_{0.53}$, and $MnFeP_{0.45}As_{0.55}$, respectively. The form of the curves collected below the Curie temperature is typical for a soft ferromagnetic material, but above the Curie temperature more complicated behavior is observed. For magnetic fields above a certain critical value, which strongly depends on temperature, the magnetization suddenly rises. This feature indicates that there is a phase transition from the paramagnetic to the ferromagnetic state triggered by the external magnetic field. The hysteresis of the magnetization isotherms reveals that the phase transition is of first order. The critical field of this phase transition rises with temperature as fast as 0.2, 0.2, and 0.175 T K^{-1} for $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$, $MnFeP_{0.47}As_{0.53}$, and $MnFeP_{0.45}As_{0.55}$, respectively. These observations agree well with the results published by other groups [29,30].

From the magnetization results, we have calculated the isothermal entropy change arising from the change of the external magnetic field under isothermal conditions up to 2 T. Results for all three samples are shown in Fig. 3. The maximum values for the entropy change are about 13, 15, and 20 J kg^{-1} K^{-1} for $MnFeP_{0.47}As_{0.53}$, $MnFeP_{0.45}As_{0.55}$, and $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$, respectively. For these calculations the validity of the Maxwell relations needs to be assumed. Utilization of this technique in the vicinity of a first-order phase transition was an object of serious criticism [31]. However, there are a number of justifications for this procedure [32,33]. Of course, we realize that the Maxwell relations can not be used strictly in the vicinity of the transition, but the experimental value of the isothermal entropy change is a mean value obtained for a whole sample. In accordance with our experimental

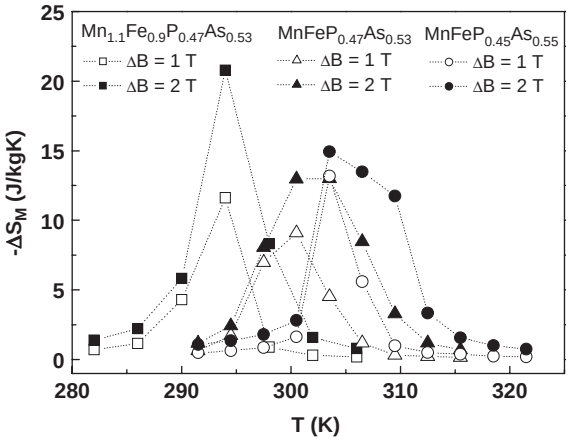

Fig. 3. Magnetic entropy changes of $MnFeP_{0.45}As_{0.55}$, $MnFeP_{0.47}As_{0.53}$, and $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$ for magnetic field changes of 0–1 and 0–2 T.

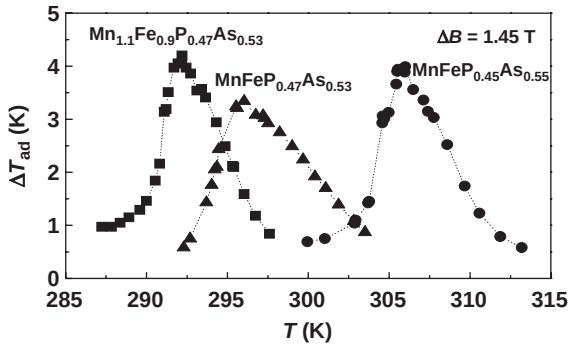

Fig. 4. Directly measured adiabatic temperature change of $MnFeP_{0.45}As_{0.55}$, $MnFeP_{0.47}As_{0.53}$, and $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$. The magnetic field grows from 0 to 1.45 T.

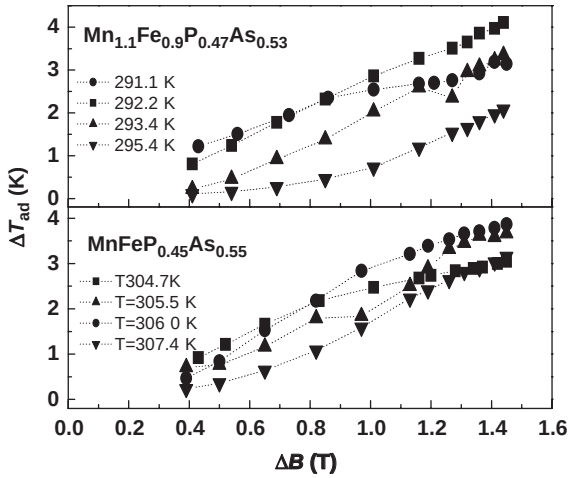

Fig. 5. Adiabatic temperature change of $MnFeP_{0.45}As_{0.55}$ and $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$ as a function of applied magnetic field. A number of curves were presented in the vicinity of T_C.

data, the phase transition does not occur at once; therefore the entropy change most likely is a continuous function of the temperature and the results of the calculations by means of the Maxwell relation may be accounted for by a sort of interpolation procedure. This procedure does not guarantee a high accuracy but provides a reasonable estimate of the exact values of the continuous function.

We also performed direct measurements of the adiabatic temperature change resulting from a fast increase of the external magnetic field. The adiabatic temperature change resulting from a field change of 1.45 T, as a function of temperature, is presented in Fig. 4. The field dependencies collected at a number of temperatures are shown in Fig. 5. The largest values of temperature change due to a magnetic field rising from 0 to 1.45 T are 4.0 K for $MnFeP_{0.45}As_{0.55}$, 3.4 K for $MnFeP_{0.47}As_{0.53}$, and 4.2 K for $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$. Data collected at 1.45 T in isothermal magnetization measurements are also plotted in Fig. 4. So we can see a good agreement between the data obtained under the different experimental conditions. The curves presented in Fig. 5 can directly be correlated with the magnetization isotherms, and the strong temperature change occurs when the magnetization curves are steep. For temperatures below T_C, dT tends to saturate and above T_C the large MCE appears only above certain values of the external magnetic field.

4. Discussion

As pointed out above, the magnetic properties observed on $MnFeP_{1-x}As_x$ prepared by solid-state reactions agree well with data published by other authors [29,30]. The behavior of the magnetization in the vicinity of the Curie temperature reveals the first-order character of the phase transition, and above the Curie temperature this transition is triggered by the external magnetic field. Looking at Fig. 5, where the MCE is plotted as a function of the external field, we can see for the experiments carried out above the temperature of the order–disorder transition that the adiabatic temperature change is very small up to a certain critical field. Therefore, we can conclude that the large values of MCE in the vicinity of the Curie temperature are directly related to the first-order phase transition. The isothermal entropy change calculated by means of the Clausius–Clapeyron relations reaches 14 J kg^{-1} K^{-1} for

$MnFeP_{0.45}As_{0.55}$, 13.2 J kg^{-1} K^{-1} for $MnFeP_{0.47}As_{0.53}$, and 13.4 J kg^{-1} K^{-1} for $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$, respectively. These values are the entropy changes directly related to the first-order phase transition itself. We find that the two former quantities are almost equal to the largest isothermal entropy change, derived by means of the Maxwell relation, but the third quantity differs in magnitude almost twice. Possibly, it means that in the two former samples the contribution of the entropy change arising from the paraprocess in the total value is considerably less than that in the third sample. Alternatively, it could mean that there is some additional source of the entropy change in the third sample as observed for a number of rare-earth-based intermetallic compounds [34].

The values observed for the isothermal entropy change are rather large. For Gd, usually considered as a model material for magnetic-refrigeration applications near room temperature, the isothermal entropy change originating from the change of the external magnetic field from zero up to 2 T is only 4 J kg^{-1} K^{-1}. In materials where a first-order phase transition is triggered by the applied magnetic field, values of up to 30 J kg^{-1} K are reported for the compound MnAs [35]. The adiabatic temperature change originating from the change of the external magnetic field reaches 2.9 K T^{-1} for pure Gd, 2.9 K T^{-1} for $La(Fe,Si)_{13}$, and 3 K T^{-1} for $Gd_5Ge_2Si_2$ and for MnAs [28,35–38]. As noted above, the isothermal entropy change for the $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$ sample is 20 J kg^{-1} K^{-1} in the magnetic field rising up to 2 T and the adiabatic temperature change is 2.9 K per 1 T. Furthermore, the curves in Fig. 5 are not saturated up to the highest field applied in our experiment, 1.45 T. This means that higher values of the adiabatic temperature change will occur for higher maximal magnetic field. As mentioned above, the first-order phase transition in MnFe(P,As) is isostructural and accompanied by only a very small volume change. This is in contrast to the structural transitions observed for $Gd_5Ge_2Si_2$ and MnAs, and the large volume change in $La(Fe,Si)_{13}$. This brings along much less thermal- and field-hysteresis for the former compounds, which can be of great significance for fast-cycling refrigerators. Furthermore, the values of the adiabatic temperature change remain stable. After 10 cycles of magnetization/demagnetization, it changes less than 1%.

The value of ΔM and ΔS depends only weakly on the concentration of Fe and Mn in the compounds $Mn_{2-x}Fe_xP_{0.5}As_{0.5}$ in the range of $x = 0.8-1.2$ and the ratio of P/As at $x = 0.35-0.65$ (see Refs. [18–20,39]). As a result our direct measurements of MCE value also demonstrate a weak concentration influence on ΔT values (see Fig. 4). Taking into account that the T_C values in the compounds can be strongly changed by changes of composition, we have the possibility of designing complex tunable working bodies which can operate in a wide temperature region without degradation of the value of the adiabatic temperature change. Because these materials exhibit only small volume changes during the phase transition and are chemically inert, these compounds can perform during long-life cycle without loss of efficiency due to structure and/or content degradation.

So we can conclude that the overall properties of the $MnFeP_{1-x}As_x$ compounds make these materials currently the most promising magnetic refrigerants in room-temperature applications.

Acknowledgments

This work has been financially supported by the Dutch Technology Foundation STW, applied science division of NWO and the Technology Program of the Ministry of Economic Affairs and Russian Foundation for Basic Research Grant No. 04-02-16709-Đ°.

References

[1] http://www.external.ameslab.gov/News/release/01magneticrefrig.htm, APS March meeting, San Antonio, TX, 2003.
[2] V.K. Pecharsky, K.A. Gschneidner Jr., Phys. Rev. Lett. 78 (1997) 4494.
[3] W. Choe, V.K. Pecharsky, A.O. Pecharsky, K.A. Gschneidner Jr., V.G. Young, G.J. Miller, Phys. Rev. Lett. 84 (2000) 4617.
[4] L. Morellon, P.A. Algarabel, M.R. Ibara, J. Blasco, B. Garcia-Landa, Z. Arnold, F. Albertini, Phys. Rev. B 58 (1998) R14721.
[5] L. Morellon, J. Blasco, P.A. Algarabel, M.R. Ibarra, Phys. Rev. B 62 (2000) 1022.
[6] A.M. Tishin, Y.I. Spichkin, Magnetocaloric effect and its applications, Series in Condensed Matter Physics, IOP publishing, Bristol, Philadelphia, 2003.
[7] X.X. Zhang, J. Tejada, Y. Xin, G.F. Sun, K.W. Wong, X. Bohigas, Appl. Phys. Lett. 69 (1996) 3596.
[8] L.E. Hueso, P. Sande, D.R. Miguens, J. Rivas, F. Rivadulla, M.A. Lopez-Quintela, J. Appl. Phys. 91 (2002) 9943.
[9] H.J. Krokozinsky, C. Santandrea, E. Gmelin, K. Barner, Phys. Stat. Sol. (b) 113 (1982) 185.
[10] T. Hashimoto, T. Numasawa, M. Shino, T. Okada, Cryogenics 21 (1981) 647.
[11] M.P. Annaorazov, M. Ünal, S.A. Nikitin, A.L. Tyurin, K.A. Asatryan, J. Magn. Magn. Mater. 251 (2002) 61.
[12] M.P. Annaorazov, K.A. Asatryan, G. Myalikgulyev, S.A. Nikitin, A.M. Tishin, A.L. Tyurin, Cryogenics 32 (1992) 866.
[13] F.X. Hu, B.G. Shen, J.R. Sun, Appl. Phys. Lett. 76 (2000) 3460.
[14] F.X. Hu, B.G. Shen, J.R. Sun, G.H. Wu, Phys. Rev. B 64 (2001) 132412.

[15] F.X. Hu, B.G. Shen, J.R. Sun, Z.H. Cheng, Phys. Rev. B 64 (2001) 012409.
[16] V.K. Pecharsky, K.A. Gschneidner Jr., A.O. Pecharsky, A.M. Tishin, Phys. Rev. B 64 (2001) 144406.
[17] L. Pytlik, A. Zieba, J. Magn. Magn. Mater. 51 (1985) 199.
[18] O. Tegus, E. Brück, K.H.J. Buschow, F.R. de Boer, Nature 415 (2002) 150.
[19] E. Brück, O. Tegus, X.W. Li, F.R. de Boer, K.H.J. Buschow, Physica B 327 (2003) 431.
[20] E. Brück, O. Tegus, L. Zhang, X.W. Li, F.R. de Boer, K.H.J. Buschow, J. Alloys Compounds, available online 24 June 2004.
[21] Y.F. Chen, F. Wang, B.G. Shen, J.R. Sun, G.J. Wang, F.X. Hu, Z.H. Cheng, T. Zhu, J. Appl. Phys. 93 (2003) 6981.
[22] Y.F. Chen, F. Wang, B.G. Shen, F.X. Hu, J.R. Sun, G.J. Wang, Z.H. Cheng, J. Phys. Condens. Matter 15 (2003) L161.
[23] Y.F. Chen, F. Wang, B.G. Shen, G.J. Wang, J.R. Sun, J. Appl. Phys. 93 (2003) 1323.
[24] S. Fujieda, A. Fujita, K. Fukamichi, Appl. Phys. Lett. 81 (2002) 1276.
[25] F. Wang, Y.F. Chen, G.J. Wang, J.R. Sun, B.G. Shen, J. Phys. Condens. Matter 16 (2004) 2103.
[26] F. Wang, Y.F. Chen, G.J. Wang, J.R. Sun, B.G. Shen, Chinese Phys. 13 (2004) 393.
[27] A.S. Chernyshov, D.A. Filippov, M.I. Ilyn, R.Z. Levitin, A.O. Pecharskaya, V.K. Pecharsky, K.A. Gschneidner, V.V. Snegirev, A.M. Tishin, Phys. Met. Metal. 93 (2002) S19.
[28] F.X. Hu, M. Ilyn, A.M. Tishin, J.R. Sun, G.J. Wang, Y.F. Chen, F. Wang, Z.H. Cheng, B.G. Shen, J. Appl. Phys. 93 (2003) 5503.
[29] R. Zach, M. Guillot, R. Fruchart, J. Magn. Magn. Mater. 89 (1990) 221.
[30] M. Bacmann, J.L. Soubeyroux, R. Barret, D. Fruchart, R. Zach, S. Niziol, R. Fruchart, J. Magn. Magn. Mater. 134 (1994) 59.
[31] A. Giguere, M. Foldeaki, B. Ravi Gopal, R. Chahine, T.K. Bose, A. Frydman, J.A. Barclay, Phys. Rev. Lett. 83 (1999) 2262.
[32] K.A. Gschneidner Jr., V.K. Pecharsky, E. Brück, H.G.M. Duijn, E.M. Levin, Phys. Rev. Lett. 85 (2000) 4190.
[33] J.R. Sun, F.X. Hu, B.G. Shen, Phys. Rev. Lett. 85 (2000) 4191.
[34] Y.I. Spichkin, A.M. Tishin, Cryogenic Engineering Conference (CEC) and International Cryogenic Materials Conference (ICMC), September 22–26, 2003, Anchorage, Alaska, USA.
[35] H. Wada, K. Taniguchi, Y. Tanabe, Mater. Trans. 43 (73) (2002).
[36] K.A. Gschneidner Jr., V.K. Pecharsky, Ann. Rev. Mater. Sci. 30 (2000) 387.
[37] K.A. Gschneidner Jr., V.K. Pecharsky, Intermetallic compounds for magnetic refrigeration, in: J.H. Westbrook, R.L. Fleischer (Eds.), Intermetallic compounds—Principles and Practice, vol. 3, Wiley, New York, 2002.
[38] S.Yu. Dan'kov, A.M. Tishin, V.K. Pecharsky, K.A. Gschneidner Jr., Phys. Rev. B 57 (1998) 3478.
[39] O. Tegus, E. Brück, X.W. Li, L. Zhang, W. Dagula, F.R. de Boer, K.H.J. Buschow, J. Magn. Magn. Mater. 272–276 (2004) 2389.