Contents lists available at ScienceDirect







journal homepage: www.elsevier.com/locate/jallcom

Field-induced reversible magnetocaloric effect in CoCl₂

X.H. Liu, W. Liu*, S. Guo, W.J. Gong, X.K. Lv, Z.D. Zhang

Shenyang National Laboratory for Materials Science and International Centre for Materials Physics, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, PR China

ARTICLE INFO

Article history: Received 22 June 2010 Received in revised form 13 July 2010 Accepted 16 July 2010 Available online 4 August 2010

Keywords: Magnetocaloric effect Field-induced transition Antiferromagnetic Ferromagnetic

1. Introduction

Due to its energy-efficient and environment-friendly features, magnetic refrigeration based on the magnetocaloric effect (MCE) has recently become a promising alternative for gas-compression refrigeration technology which is presently widely used [1–7]. Up to now, the MCE has been used in magnetic refrigerant devices mainly in the low-temperature range by using the paramagnetic (PM) salt $Gd_3Ga_5O_{12}$ (T < 20 K) [8]. Therefore, it is of interest to explore magnetic refrigerant materials with a large MCE in other temperature ranges. Usually, a large MCE can be obtained near the magnetic-ordering temperature due to an external magnetic field greatly influences the spin ordering, while a giant-MCE is found to relate with a field-induced first-order magnetic transition [9–13]. However, a first-order magnetic transition usually gives rise to considerable thermal/magnetic hysteresis which is disadvantageous for application. Therefore, much attention has been recently focused on finding new materials with a large MCE and a small thermal/magnetic hysteresis. Furthermore, as the thermal/magnetic hysteresis is quite small for antiferromagnetic (AF) systems, compared with giant-MCE ferromagnetic (FM) materials, they may be more suitable for application on the aspect of refrigerant efficiency and energy conservation. Cobalt chloride CoCl₂·6H₂O is an AF material with Néel temperature of 2.29K [14]. However, the AF CoCl₂ has Néel temperature of 24.9 K, in which the exchange interaction between Co²⁺ ions is isotropic in the ionic

ABSTRACT

A sign change of the magnetocaloric effect is induced by a magnetic field, which is related to a fieldinduced transition from the antiferromagnetic to the ferromagnetic state below the Néel temperature of CoCl₂ nanoparticles. The reversible magnetic-entropy change $-\Delta S_m$ (4.1 and 11.5 Jkg⁻¹ K⁻¹ at 27 K for a field change of 3 and 7T, respectively) almost without hysteresis and the large cooling power (83.4 and 148 Jkg⁻¹, correspondingly) indicates that CoCl₂ is a potential candidate for application in magnetic refrigeration in the low-temperature range.

© 2010 Elsevier B.V. All rights reserved.

spins [15]. The electronic structure and magnetic properties of CoCl₂ have been investigated by several groups [16–19], but the magnetocaloric effect was not reported. In this work, we study the magnetic and magnetocaloric properties of the antiferromagnet CoCl₂ at low temperatures. A negative magnetic-entropy change and a large cooling power are found together with a field-induced MCE conversion (the MCE changes its sign in the applied magnetic field).

2. Experimental

CoCl₂ was fabricated by following method. The cobalt chloride CoCl₂·6H₂O of 99% purity was dried at 373 K for 20 h in air to obtain CoCl₂ powder. The X-ray diffraction pattern confirms the almost single-phase state of the powder, crystallizing in the hexagonal CdCl₂-type structure (space group $R\bar{3}m$), and the lattice parameters a and c is 3.553 and 17.35 Å, respectively. The orientation of Co²⁺ moments is perpendicular to the hexagonal *c*-axis [20]. The average grain size of the powder was determined to be about 40 nm by the Scherrer formula [21]. The magnetization data were measured by using a superconducting quantum interference device magnetometer from 4 to 300 K at applied fields up to 7T. The powder was fixed by paraffin in a capsule in order to immobilize the randomly oriented particles during the measurements.

3. Results and discussion

The temperature dependences of the magnetization in zerofield-cooling (ZFC) (solid circle) and field-cooling (FC) (half circle) from 4 to 300 K with applied field of 0.01 T are shown in Fig. 1. It is found that the sample exhibits transition from paramagnetic (PM) to AF at the Néel temperature of around 22 K (as the arrow indicates), slightly lower than the value of 24.9 K reported in Ref. [15], which may be due to the decrease of the grain size of CoCl₂. In other words, the transition temperature of nanoparticles decreases

^{*} Corresponding author. Tel.: +86 24 83978856; fax: +86 24 23891320. *E-mail address:* wliu@imr.ac.cn (W. Liu).

^{0925-8388/\$ -} see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2010.07.180



Fig. 1. Temperature dependences of the magnetization in zero-field-cooling (ZFC) (solid circle) and field-cooling (FC) (half circle) from 4 to 300 K of $CoCl_2$, measured at an applied magnetic field of 0.01 T. Inset: Hysteresis loop at 5 K in an applied field of 5 T, the arrow indicates the field-induced transition from AF to FM.

as compared with that of the bulk [22,23]. The inset of Fig. 1 presents the magnetic hysteresis loop at 5 K in an applied field of 5 T. It can be noticed that the coercivity is extremely small (only about 0.005 T) and the remanent magnetization is close to zero. Furthermore, there is nearly zero magnetic hysteresis in the transition field (as the arrow indicates). Compared with typical giant-MCE materials (such as $Gd_5(Ge_{1-x}Si_x)_4$ [10], in which the magnetic hysteresis is about 1 T near the magnetic-transition temperature), the small magnetic hysteresis of $CoCl_2$ is advantageous for application at low temperatures.

Fig. 2 represents the magnetization curves of CoCl₂ between 4 and 42 K with ΔT = 2 K. Below T_N , the magnetization increases gradually with the applied field in the low field range, and then jumps at a critical field, but unsaturated even at 7T. The step in the magnetization curves clearly indicates a field-induced AF to FM phase transition. The critical magnetic field B_c (determined by the maximum of dM/dB) is about 1.7 T. The M-B curve at 6 K in an applied field of 7 T and the values of dM/dB dependence of B are presented in Fig. 3(a) and (b), respectively. It can be found that the AF CoCl₂ is a metamagnetic state at low temperature in applied field, and the direction of spins can be changed by relatively large applied field of about 1.7 T, which is different from the conventional AF materials (such as NiO or CoO). Mills [24] reported that the field applied parallel to the direction of the easy magnetization direction of AF sublattice may lead to the instability of the ground state of AF material, if the strength *B* exceeds the critical field *B*_c. The metamagnetic transition was not found in some AF materials, which may be due



Fig. 2. Magnetic isotherms of CoCl₂, measured between 4 and 42 K with a temperature step of 2 K.



Fig. 3. The *M*–*B* curve at 6 K in an applied field of 7 T (a), and the values of dM/dB dependence of field *B* (b). The directions of two sublattice spins of the AF CoCl₂ dependence of applied field are simply indicated by arrows in (a).

to large B_c greatly exceeds the applied field [25]. The directions of the two sublattice spins at applied field are illustrated in Fig. 3(a) by arrows [26]. However, as our sample is powder, it is very difficult to observe the sharp transition from AF to FM as in a single crystal.

In order to further understand this magnetic transition, the temperature dependence of the magnetization M(T) in different applied fields (1, 1.3, 1.7, 2.5, 3.1 T) is plotted in Fig. 4 (temperature range from 4 to 42 K with $\Delta T = 2$ K). It is found that the T_N at around 22 K in a low field is consistent with Fig. 1. A field-induced transition from AF to FM state below T_N is observed. The critical magnetic field (determined from the maximum of dM/dB) for this transition is about 1.7 T. A peak corresponding to T_N is observed at low field (B < 1.7 T), which disappears at high fields with negative slopes of magnetization. Moreover, the transition temperature shifts to low temperatures with increasing applied field (as dashed line indicates).

A large MCE is expected around T_N where the magnetization rapidly changes with varying temperature. The isothermal entropy change was derived from the magnetization data by means of the expression $\Delta S_m(T, B) = \int_0^B (\delta M / \delta T) dB$ that can be obtained from the



Fig. 4. Temperature dependence of the magnetization at different magnetic fields (1, 1.3, 1.7, 2.5, and 3.1 T) obtained from M(B) data shown in Fig. 2. The dashed line indicates that the transition temperatures shift to low temperatures with increasing field *B*.



Fig. 5. Negative magnetic-entropy change, $-\Delta S_m$, of CoCl₂ as a function of temperature for different magnetic field changes (ΔB). Inset: d*M*/d*T* versus *T* at 1, 1.7 and 3.1 T.

Maxwell relation. The curves of $-\Delta S_m$ versus *T* in different applied fields are given in Fig. 5. The inset shows the d*M*/d*T* versus *T* in applied field of 1, 1.7, 3.1 T. The minimum of d*M*/d*T* at around 27 K for different field indicates the large MCE at this temperature. Furthermore, for small magnetic field (2.1 T), $-\Delta S_m$ is negative (inverse MCE) below T_N , whereas it changes to small positive values with increasing temperature. Usually, the inverse MCE is observed in first-order magnetic transitions such as AF/FI [27], AF/FM [28]. The inverse MCE has also been reported in AF/PM transition systems [29], in which the applied field results in a spin-disordered state near the transition temperature, which leads to increase of the entropy [6]. When the applied magnetic field is higher than 3 T, a positive cusp-shape $-\Delta S_m$ with peak position at 27 K is observed, which is consistent with the minimum value of d*M*/d*T* (see the inset of Fig. 5).

The applied field destroys the antiparallel alignment of the spin moments, and the spin disorder results in a negative $-\Delta S_{\rm m}$, becoming more negative with increasing applied field. However, the value of $-\Delta S_{\rm m}$ increases with further increasing magnetic field, due to the field-induced transition from the AF to the FM state, and becomes positive at 3.1 T. Thus, clearly, the field-induced AF to FM transition is responsible for the conversion from the inverse to the conventional MCE in CoCl₂. The maximum of $-\Delta S_{\rm m}$ of 4.1 and 11.5 J kg⁻¹ K⁻¹ at 27 K for ΔB = 3 and 7 T, respectively. The slope of the curve in Fig. 5 is relatively small, and the smooth variation of $-\Delta S_{\rm m}$ with temperature is more useful than a sharp one, which is another property of CoCl₂ that makes it a promising magnetore-frigerant.

The relative cooling power $-\Delta S_{maxM} \delta T_{fwhm}$ is a measure of how much heat can be transferred between cold and hot sinks in an ideal refrigerant cycle, which is of practical significance [30]. Here δT_{fwhm} is the full width at half maximum $-\Delta S_m$, namely, temperature interval at half values of the peak of the magnetic-entropy change. The cooling power of CoCl₂ calculated is about 83.4 and 148 J kg⁻¹ for a magnetic field change from 0 to 3 T and from 0 to 7 T, respectively.

4. Conclusion

A field-induced MCE conversion is observed in CoCl₂ associated with the field-induced transition from the AF to FM states. The value of magnetic-entropy change (4.1 and $11.5 J kg^{-1} K^{-1}$ at 27 K for a field change of 3 and 7 T) and cooling power (83.4 and 148 J kg⁻¹, correspondingly) and nearly no thermal/magnetic hysteresis make CoCl₂ a potential material for magnetic refrigeration in the low-temperature range.

Acknowledgements

This work has been supported by the National Nature Science Foundation of China under projects 50831006 and 50971123 and National Basic Research Program (No. 2010CB934603) of China, the Ministry of Science and Technology of China.

References

- [1] C.B. Zimm, A. Jastrab, A. Sternberg, V.K. Pecharsky, K.A. Gschneidner Jr., M. Osborne, I. Anderson, Adv. Cryog. Eng. 43 (1998) 1759.
- [2] J. Glanz, Science 279 (1998) 2045.
- [3] K.A. Gschneidner Jr., V.K. Pecharsky, A.O. Tsokol, Rep. Prog. Phys. 68 (2005) 1479.
- [4] E. Brück, O. Tegus, D.T.C. Thanh, K.H.J. Buschow, J. Magn. Magn. Mater. 310 (2007) 2793.
- [5] A. De Campos, D.L. Rocco, A.M.G. Carvalho, L. Caron, A.A. Coelho, S. Gama, L.M. da Silva, F.C.G. Gandra, A.O. dos Santos, L.P. Cardoso, P.J. von Ranke, N.A. de Oliveira, Nat. Mater. 5 (2006) 802.
- [6] T. Krenke, E. Duman, M. Acet, E.F. Wassermann, X. Moya, L. Manosa, A. Planes, Nat. Mater. 4 (2005) 450.
- [7] X.H. Liu, W. Liu, W.J. Hu, S. Guo, X.K. Lv, W.B. Cui, X.G. Zhao, Z.D. Zhang, Appl. Phys. Lett. 93 (2008) 202502.
- [8] J.A. Barclay, W.A. Steyert, Cryogenics 22 (1982) 73.
- [9] O. Tegus, E. Brück, K.H.J. Buschow, F.R. de Boer, Nature (London) 415 (2002) 150.
- [10] V.K. Pecharsky, K.A. Gschneidner Jr., Phys. Rev. Lett. 78 (1997) 4494.
- [11] S. Gama, A.A. Coelho, A. de Campos, A.M.G. Carvalho, F.C.G. Gandra, P.J. von Ranke, N.A. de Oliveira, Phys. Rev. Lett. 93 (2004) 237202.
- [12] H. Wada, Y. Tanabe, Appl. Phys. Lett. 79 (2001) 3302.
- [13] F.X. Hu, B.G. Shen, J.R. Sun, Z.H. Cheng, G.H. Rao, X.X. Zhang, Appl. Phys. Lett. 78 (2001) 3675.
- [14] I.J. Lowe, D.W. Whitson, Phys. Rev. B 6 (1972) 3262.
- [15] J.E. Kardontchik, E. Cohen, J. Makovsky, Phys. Rev. B 16 (1977) 508.
- [16] S. Antoci, L. Mihich, Phys. Rev. B 21 (1980) 3383.
- [17] H. Zabel, S.M. Shapiro, Phys. Rev. B 36 (1987) 7279.
- [18] I.S. Suzuli, T.Y. Huang, M. Suzuki, Phys. Rev. B 65 (2002) 224432.
- [19] M. Suzuki, I.S. Suzuli, M. Matsuura, Phys. Rev. B 73 (2006) 184414.
- [20] M.K. Wilkinson, J.W. Cable, E.O. Wollan, W.C. Koehler, Phys. Rev. 113 (1959) 497.
- [21] H.P. Klug, L.E. Alexander, X-ray Diffraction Procedures for Poly-crystalline and Amorphous Materials, 2nd ed., Wiley, New York, 1974 (chapter 9).
- [22] X.H. Liu, W.B. Cui, X.K. Lv, W. Liu, X.G. Zhao, D. Li, Z.D. Zhang, J. Phys. D: Appl. Phys. 41 (2008) 105005.
- [23] J. Nogués, J. Sort, V. Langlais, V. Skumryev, S. Suriñach, J.S. Muñoz, M.D. Baró, Phys. Rep. 422 (2005) 65.
- [24] D.L. Mills, Phys. Rev. Lett. 20 (1968) 18.
- [25] X.H. Liu, W. Liu, X.K. Lv, F. Yang, X. Wei, Z.D. Zhang, D.J. Sellmyer, J. Appl. Phys. 107 (2010) 083919.
- [26] K.H.J. Buschow, F.R. de Boer, Physics of Magnetism and Magnetic Materials, 3rd ed., Kluwer Academic/Plenum Publishers, New York, 2003 (chapter 4).
- [27] O. Tegus, E. Brück, L. Zhang, K.H.J. Buschow, F.R. de Boer, Phys. B 319 (2002) 174.
- [28] M.P. Annaorazov, S.A. Nikitin, A.L. Tyurin, K.A. Asatryan, A.K. Dovletov, J. Appl. Phys. 79 (1996) 1689.
- [29] W.J. Hu, J. Du, B. Li, Q. Zhang, Z.D. Zhang, Appl. Phys. Lett. 92 (2008) 192505.
- [30] W.F. Giauque, D.P. Macdougall, Phys. Rev. 43 (1933) 768.