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LETTER TO THE EDITOR

A potential oxide for magnetic refrigeration application: CrO_2 particles

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Abstract

The magnetocaloric effect (MCE) of half-metallic CrO_2 particles has been studied with respect to particle size on the nanometre scale. Results from superconducting quantum interference device (SQUID) measurements indicate that acicular CrO_2 particles with a length of 400 nm yield a large magnetic entropy change ΔS_M of 5.1 J kg^{-1} K^{-1} at an applied field of 15 kOe and an adiabatic temperature change ΔT_{ad} of 2.0 K near the Curie temperature ($\sim$390 K). These results are among the highest for magnetic oxides, and are comparable to that for pure Gd. However, smaller CrO_2 particles with a length of 260 nm only exhibit $\Delta S_M = 2.25$ J kg^{-1} K^{-1} and $\Delta T_{ad} = 0.95$ K. The difference in MCE between these two sizes of CrO_2 particles results primarily from disordered spins on the surface of the particles. In addition, measurements and calculations of the specific heat capacity for the CrO_2 particles are presented. These results indicate that the total specific heat capacity is dominated by the magnetic specific heat contribution. Therefore, we believe that these CrO_2 nanoparticles may hold future promise in the development of new magnetic refrigerants.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Solid materials for magnetic refrigeration have been attracting considerable attention due to several advantages over conventional gas refrigerants, i.e. solid-state refrigerants are likely

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to have high energy efficiency, small volume, and fewer pollution problems [1]. Therefore, magnetic materials with a large magnetocaloric effect (MCE) are expected to be useful for next-generation magnetic refrigerator. In general, for a given material, two major parameters are used to evaluate quantitatively how efficiently a material produces the magnetocaloric effect. One is the magnetic entropy change ΔS_M, and another is the adiabatic temperature change ΔT_{ad}. In addition, it is usually important to measure the temperature dependence of ΔS_M and/or ΔT_{ad} in different external fields. At equilibrium, MCE is correlated with the magnetization (M), magnetic field (H), heat capacity (C) and absolute temperature (T) and can be described by the following Maxwell equations:

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

$$\Delta T_{ad}(T, \Delta H) = T(S, H) - T(S, 0) = -\int_0^H \left(\frac{T}{C(T, H)} \times \frac{\partial M(T, H)}{\partial T}\right)_H \mathrm{d}H. \tag{2}$$

Apparently, both of these equations are of significance in understanding the MCE in solids.

Recently, much effort has been directed at discovering new magnetic refrigerant materials. Some possible candidates include the rare-earth element Gd [2], $Gd_5(Ge_{1-x}Si_x)_4$ ($0 \leqslant x \leqslant 0.5$) [3], $MnAs_{1-x}Sb_x$ ($0 \leqslant x \leqslant 0.4$) alloys [4], and manganite oxides $Ln_{1-x}R_xMnO_3$ (Ln = La, Nd, Pr, Sm, etc and R = Ca, Sr, Ba, Pb, etc) [5, 6] etc. But in most of these studies, the materials required a high external field (several tesla) to yield high cooling efficiency. This severely hinders development of the materials as magnetic refrigerants for practical applications. Due to their easily tunable phase transition temperature and small hysteresis loss, manganite oxides have been widely studied in the past several years. However, no other oxides have been useful for magnetic refrigeration applications so far [7].

Although CrO_2 has been widely used as a magnetic recording material, it has aroused a hot debate on spintronics device applications in recent years. Due to near 100% spin polarization at the Fermi level, CrO_2 is a likely spintronic material [8]. Our previous work showed that CrO_2 particles can give rise to a large magnetoresistance (MR) of -25% at a low magnetic field of 10 kOe [9], and a large room-temperature MR can be measured for polymer-coated CrO_2 particles [10]. In this letter, the MCE for CrO_2 particles with different sizes is investigated. This work includes measurement, calculation and discussion of magnetization, magnetic entropy and adiabatic temperature change, as well as specific heat for the unique half-metal magnet. The experiment presents an intriguing fact that CrO_2 with a large size (400 nm length) can exhibit a large MCE at a low magnetic field, uncovering a new class of potential magnetic refrigerants.

2. Experiment

The raw CrO_2 particles (sample C400) supplied by Micro Magnetics Inc., USA, are acicular single-domain particles with an average length of 400 nm and an aspect ratio of about 9:1. The raw particles were ground for 300 h by ball milling until the final length of the particles is about 260 nm (sample C260). The detailed static magnetic property of the two samples is reported in [11]. The size and shape of the particles were determined using transmission electron microscopy (TEM). The phase and crystal structure of the samples were characterized using a Rigaku D/MAX-2500C x-ray diffraction (XRD) apparatus utilizing a Cu Kα radiation source. The temperature dependence of the magnetic properties was measured using a superconducting quantum interference device (SQUID) Quantum Design MPMS over a temperature range from 300 to 450 K.

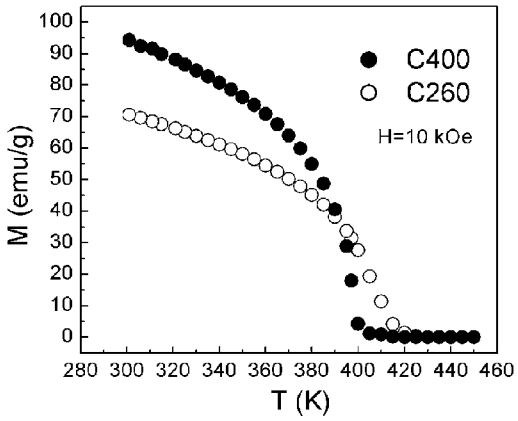

Figure 1. Magnetization of CrO_2 as a function of temperature at a magnetic field of 10 kOe for samples C400 and C260.

3. Results and discussion

Figure 1 presents the temperature dependence of magnetization for sample C400 and C260 from 300 to 450 K at a magnetic field of 10 kOe. The magnetization for both the samples drops rapidly at the Curie temperature, T_C, where they exhibit a sharp phase transition from ferromagnetism to paramagnetism. Here, the Curie temperature T_C is 396 and 405 K for samples C400 and C260, respectively. It is noticed that the CrO_2 particles with small size (C260) have a low specific magnetization and high T_C, compared to those for the sample C400. The reduction in magnetization results primarily from the increase in specific surface area for the small-size particles (C260), whereas the strong coupling between the ferromagnetic CrO_2 and antiferromagnetic Cr_2O_3 (natural layer) on the surface of the CrO_2 particles may lead to an increase in the Curie temperature [9]. It is worth mentioning that an abrupt jump in magnetization with respect to temperature appears in the vicinity of the magnetic phase transition, which may be responsible for the large MCE in the material.

The isothermal magnetization for samples C400 and C260 is measured over a field range of 0–15 kOe and a temperature range of 300–450 K, as depicted in figure 2. Prior to each measurement of isotherm magnetization, the samples are heated above T_C and then cooled down to the measured temperature with no applied field. Such measurements are acceptable for an isothermal magnetization process, since a sufficiently low sweep rate of the magnetic field is applied in the measurement. As illustrated, the largest change in magnetization occurs over temperature ranges of 380–400 K and 380–410 K for the samples C400 and C260, respectively. This also coincides completely with the results shown in figure 1. More importantly, a marked change in magnetization for sample C400 only occurs at relatively low fields (<2 kOe), which is very useful for applications of this low-field MCE material.

Figure 3 shows the magnetic entropy change, ΔS_M, as a function of temperature at different magnetic fields for the two samples, which is derived from equation (1). The maximum ΔS_M for both of the samples appears near the Curie temperature T_C. As expected, the CrO_2 particles demonstrate an extremely large low-field magnetic entropy change of $\Delta S_M = 5.1$ J kg^{-1} K^{-1} at $H = 15$ kOe for sample C400, whereas sample C260 has a smaller $\Delta S_M = 2.25$ J kg^{-1} K^{-1}. The results are impressive and represent one of the largest MCEs ever observed in magnetic oxides [7]. Actually, the ΔS_M of sample C400 is comparable to that of pure Gd (4.2 J kg^{-1} K^{-1}) magnetic refrigerants. Moreover, the maximum magnetic entropy

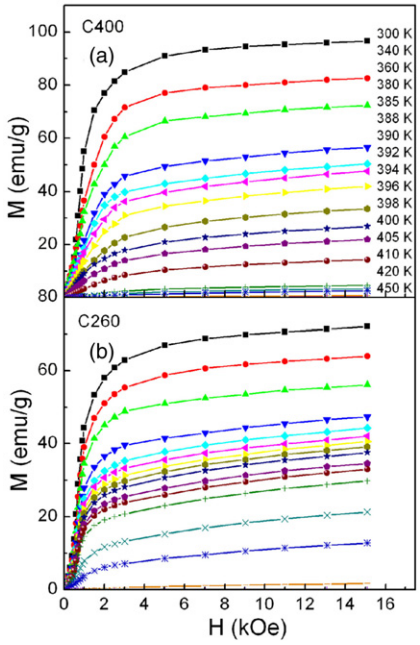

Figure 2. Isothermal M–H curves of CrO_2 at different temperatures ranging from 300 to 450 K: (a) sample C400 and (b) sample C260.

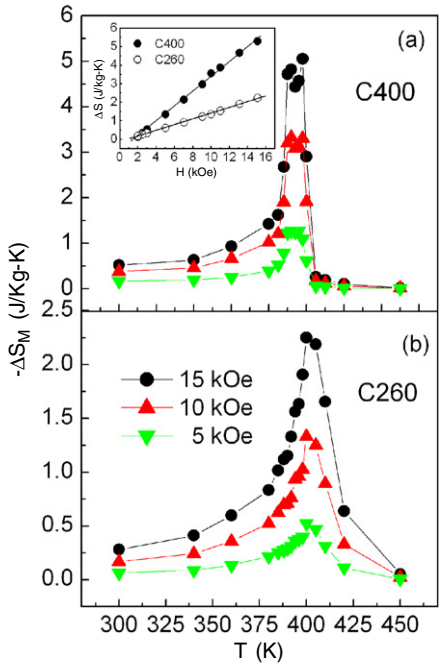

Figure 3. Temperature dependence of magnetic entropy change (ΔS_M) of CrO_2 at magnetic fields of 15, 10, and 5 kOe: (a) sample C400; (b) sample C260. The inset of (a) shows the maximum $|\Delta S_M|$ as a function of magnetic field. The straight lines are guides for the eye.

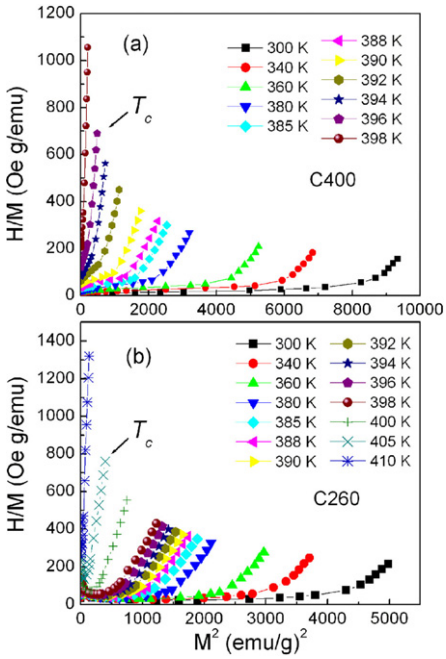

Figure 4. H/M versus M^2 plots of CrO_2 at different temperatures for CrO_2 particles: (a) sample C400; (b) sample C260.

change ΔS_M for both the samples shows a linear increase ($\Delta S_M = p + kH$) with increasing magnetic field, as shown in the inset of figure 3(a). Clearly, a large slope is associated with the larger particles of the sample C400, whereas sample C260 exhibits a smaller ΔS_M and a broadened peak of ΔS_M.

An early attempt was made to model the magnetocaloric effect theoretically in terms of Weiss molecular mean field theory for lanthanum manganites [12]. Unfortunately, the model has not led to very good agreement between theoretical and experimental results. Most recently, a Landau-based theory has been used successfully to describe magnetic properties and phase transitions for some manganites. This theory has been especially useful for describing the temperature dependence of the magnetic entropy change for the manganites [13]. Accordingly, the Gibbs free energy G_F is expressed as

$$G_F(T, M) = G_0 + \tfrac{1}{2}AM^2 + \tfrac{1}{4}BM^4 - MH, \tag{3}$$

where the coefficient A and B are temperature-dependent parameters. On the condition of equilibrium, $\frac{\partial G_F}{\partial M} = 0$, equation (3) can be simplified as

$$H/M = A + BM^2. \tag{4}$$

Thus, the type of magnetic transition for the present samples can be determined using the Banerjee criterion [14]. When the slope of the H/M versus M^2 plot is negative, the system possesses a first-order magnetic phase transition. On the other hand, a positive slope corresponds to a second-order magnetic phase transition. Apparently, the CrO_2 particles have a second-order magnetic phase transition at T_C due to the observed positive slope, as shown in figure 4. Theory predicts that the second-order phase transition may result in a large magnetic entropy change over a broad temperature range [15], which is consistent with our experiment result (a temperature span of ~20 K), as shown in figure 3.

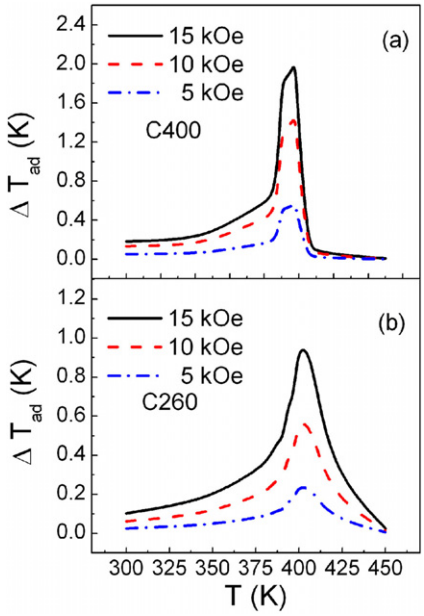

Figure 5. Temperature dependence of adiabatic temperature change (ΔT_{ad}) of CrO_2 at different magnetic fields.: (a) sample C400; (b) sample C260.

Another important evaluation of the magnetocaloric effect is the adiabatic temperature change ΔT_{ad}. Magnetic entropy is reduced with increasing magnetic field due to an increase in magnetic order. Thus, the magnetic material is heated when $\Delta T_{ad}(T, \Delta H)$ is positive, combining with a negative $\Delta S_M(T, \Delta H)$. An approximate estimation of adiabatic temperature change can be performed by the measured ΔS_M as

$$\Delta T_{ad} = -\Delta S_M \frac{T}{C(T, H)}. \tag{5}$$

The specific heat $C(T, H)$ in equation (5) is considered to be the sum of the lattice and magnetic contribution, namely $C(T, H) = C_D + C_M$. The Debye specific heat C_D is calculated from

$$C_D = 9k_B N \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{e^x x^4}{(e^x - 1)^2} dx \tag{6}$$

where k_B is the Boltzmann constant, N is the number of atoms per unit mass, and $\theta_D = 593$ K is the Debye temperature for CrO_2 [16]. The magnetic contribution to the specific heat capacity C_M is given by the derivative of the magnetization with respect to temperature,

$$C_M = -H_{ext}\frac{\partial M}{\partial T} - \frac{1}{2}H_{int}\frac{\partial M^2}{\partial T}. \tag{7}$$

Here, $H_{int} = \frac{3k_B T_c}{N_s g^2 \mu_B^2 J(J+1)}$ is the mean field constant, and N_s is the number of spins per unit mass. The g is the Lande factor and J is the total angular momentum. The estimated adiabatic temperature change ΔT_{ad} for the two samples is illustrated in figure 5. The maximum ΔT_{ad} achieved is 2.0 and 0.95 K at a magnetic field of 15 kOe for the samples C400 and C260, respectively. In particular, such an adiabatic temperature change ΔT_{ad} ($\sim$2.0 K) for sample C400 is $\sim$48% of ΔT_{ad} (=4.2 K) for pure Gd, and also represents one of the largest adiabatic

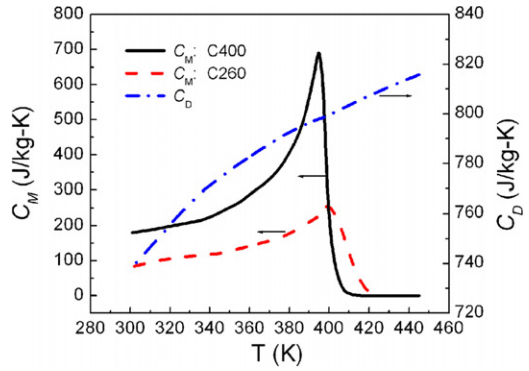

Figure 6. Variation of specific heat capacities C_D and C_M (H_{ext} = 15 kOe) of CrO_2 with temperature for samples C400 and C260.

temperature changes ever reported for oxides [12, 17, 18]. The quantitative correlation between ΔS_M and ΔT_{ad} was discussed in [19]. The behaviour of $\Delta T_{ad}(T)_{\Delta H}$ is assumed to be quite similar to $|\Delta S_M(T)_{\Delta H}|$, i.e. either ΔT_{ad} or ΔS_M is gradually reduced when the temperature is below or above the Curie temperature T_C. This assumption is in good agreement with our observations, as shown in figure 5.

The contribution of lattice heat capacity C_D and magnetic heat capacity C_M to the total heat capacity can be separated from equations (6) and (7), as shown in figure 6. Here, we suppose that the two samples have the same Debye temperature, θ_D, and number of atoms per unit mass, N. Thus, the values of C_D are the same for these samples as well. As illustrated in figure 6, the change in C_D from 300 to 400 K is $\Delta C_D = 60.8\ \mathrm{J\,kg^{-1}\,K^{-1}}$. In contrast, the maximum variation of C_M at $H = 15$ kOe in the ferromagnetic region is $\Delta C_M = 376.9\ \mathrm{J\,kg^{-1}\,K^{-1}}$ and $115.1\ \mathrm{J\,kg^{-1}\,K^{-1}}$ for samples C400 and C260, respectively. These results indicate that the magnetic heat capacity C_M dominates changes in the adiabatic temperature for the CrO_2 particles.

By comparing the MCE of the two samples with different particle sizes, it is found that both ΔS_M and ΔT_{ad} are lower for smaller-size particles, such as sample C260. Since the magnetic entropy change for the samples results mainly from the field-induced spin alignment near the magnetic phase transition temperature, the reduction in either ΔS_M or ΔT_{ad} is due to the contribution of the disordered spins on the surface of the CrO_2 particles. We estimate the specific surface area (σ) for both samples, assuming a cylinder of CrO_2 with lengths of 400 and 260 nm and diameters 44.4 and 28.8 nm, respectively. Thus, the ratio of specific surface area of the two samples is $\sigma(\mathrm{C400})/\sigma(\mathrm{C260}) = 0.64$, which is found to be comparable to the ratio of magnetic entropy change $\Delta S_M(\mathrm{C260})/\Delta S_M(\mathrm{C400}) = 0.43$. Thus, it is reasonable to expect that smaller particles having larger specific surface area may give rise to a lower MCE due to more disordered spins per unit volume. Similar results are also observed in $La_{0.75}Ca_{0.25}MnO_3$ [20]. Furthermore, we assume that an even larger low-field MCE may be achieved for single-crystal oxides, as opposed to polycrystalline particles. The work on $La_{0.69}Ca_{0.31}MnO_3$ [21] and $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ [22] provides powerful evidence to support the assumption above.

4. Conclusions

In summary, we have completed a detailed investigation of magnetic entropy changes, ΔS_M, and adiabatic temperature changes, ΔT_{ad}, for half-metallic CrO_2 particles. A large low-

field magnetocaloric effect is clearly observed for the particles, which originates from a large spontaneous magnetization and a quick reduction in magnetization. The CrO_2 acicular particles with 400 nm length and 45 nm diameter yield a large magnetic entropy of 5.1 J kg^{-1} K^{-1} and adiabatic temperature change of 2.0 K at an applied field of 15 kOe, whereas a smaller particle size exhibits smaller magnetic entropy and adiabatic temperature change. The decreases in ΔS_M and ΔT_{ad} are associated with an increase in disordered surface spins. In addition, analysis of the specific heat capacity indicates that the magnetic specific heat is the dominant contribution to total heat capacity for the material. Therefore, we believe that these nanoparticles may open up a new application of CrO_2 materials, in addition to magnetic recording and spintronics applications.

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