Communication

Large room-temperature rotating magnetocaloric effect in NdCo$_4$Al polycrystalline alloy

Y. Hu [a,b], Q.B. Hu [a,b], C.C. Wang [a,b], Q.Q. Cao [a,b], W.L. Gao [b], D.H. Wang [a,b,*], Y.W. Du [a,b]

[a] National Laboratory of Solid State Microstructures and Jiangsu Key Laboratory for Nano Technology, Nanjing University, Nanjing 210093, China
[b] School of Physics, Nanjing University, Nanjing 210093, China

A B S T R A C T

The magnetic refrigeration based on rotating magnetocaloric effect (MCE) is promising to build a simplified magnetic cooling system. Until now, most magnetic refrigerants for rotating MCE are single crystal and work at low temperature, which hinder the development of this refrigeration technology. In present paper, we report a large room-temperature rotating MCE in a magnetic-field-aligned NdCo$_4$Al polycrystalline alloy. A large rotating magnetic entropy change of 1.3 J kg^{-1} K^{-1} under 10 kOe and a broad operating temperature window of 52 K are achieved. The origin of large rotating MCE in NdCo$_4$Al polycrystalline alloy and its advantages for rotating magnetic refrigeration are discussed.

1. Introduction

The magnetocaloric effect (MCE) refers to the temperature change in a magnetic material caused by an external magnetic field change in the adiabatic process. The magnetic refrigeration based on MCE is an attractive cooling technology for its environmental safety and high efficiency, which could potentially replace the common vapor compression cycle technology in use nowadays. For conventional working method of magnetic refrigeration, the magnetocaloric materials need to be moved in and out of the magnetic field zone, which requires a large working space. Recently, an alternative magnetic refrigeration concept, rotating MCE, has been proposed, which is promising to solve this problem [1–6]. The schematic of the implementation of rotating MCE is shown in Fig. 1(a). Magnetic refrigeration can be realized by rotating refrigerants in a constant magnetic field zone instead of moving them in and out of the magnetic field zone, which offers the possibility to build a simplified and compact magnetic cooling system. According to the working principle of rotating MCE, the refrigerant should show different values of MCE with the variation of magnetic field direction, i.e. anisotropic MCE. Up to now, large rotating MCE has been observed in some single crystals, such as HoMn$_2$O$_5$ [3], TmMnO$_3$ [4], and ErFeO$_3$ [5], due to strong magnetocrystalline anisotropy (MCA) of rare earth ions. However, the operating temperature of most of them are far below room temperature [3–5,7], which hinders their applications for the household appliances. Recently, a giant rotating MCE has been reported in NdCo$_5$ single crystal, which peak temperature of rotating MCE is close to the room temperature [2]. However,

from the practical application point of view, the working temperature of this magnetic refrigerant needs to be further increased. Besides, the high cost and complexity of preparation for single crystal is another hurdle that should be overcome to fulfill NdCo$_5$ for rotating magnetic refrigeration.

NdCo$_5$ is a ferromagnetic intermetallic compound which crystallizes in a hexagonal CaCu$_5$-type structure with $P6/mmm$ space group. In this alloy, MCA of Co sublattice favors the c axis (first-order anisotropic constant K_{1Co} >0), while the Nd sublattice tends to have a planar (ab plane) MCA (K_{1Nd} <0). Due to the existence of these two types of MCA and the competition between them, NdCo$_5$ would undergo two second-order spin-reorientation (SR) transitions at T_{SR1}=250 K and T_{SR2}=290 K, respectively [8–14]. It is reported that partial substitution of Al for Co in NdCo$_5$ would remarkably increase the SR temperature, which is attributed to the modification of magnetic anisotropy by Al-doping [15–18]. In addition, the magnetic-field-aligned technology is proved to be an effect approach to achieve textured polycrystalline compounds, which can show large MCA as well [15,16,19]. Based on this method, we prepare an orientated NdCo$_4$Al polycrystalline alloy and investigate its rotating MCE. The experimental results indicate that this magnetic-field-aligned alloy has a large low-field rotating MCE at room temperature.

2. Experimental

Polycrystalline sample of NdCo$_4$Al was prepared by arc melting the stoichiometric amount of the high purity elements. For a better

* Corresponding author at: National Laboratory of Solid State Microstructures and Jiangsu Key Laboratory for Nano Technology, Nanjing University, Nanjing 210093, China.
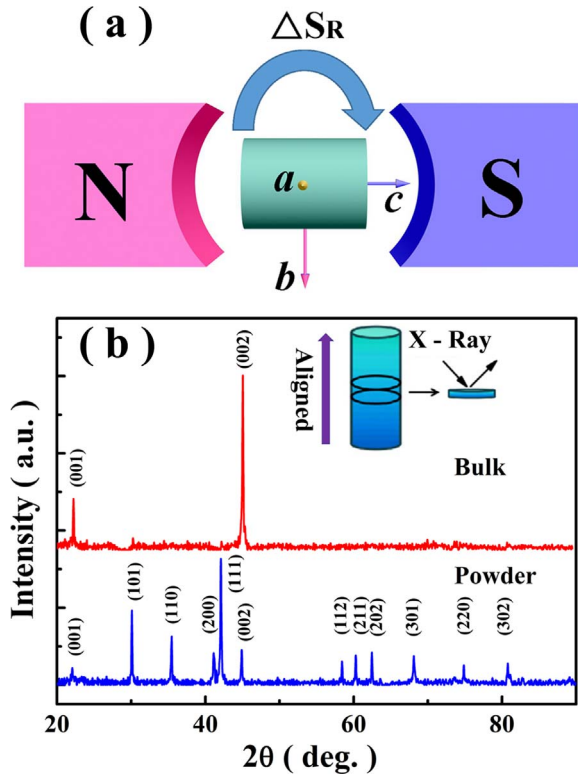 *E-mail address:* wangdh@nju.edu.cn (D.H. Wang).

Fig. 1. (Color online) (a) A schematic for the implementation of the rotating MCE by rotating.refrigerants in a constant magnetic field, (b) X-ray diffraction patterns of a field-oriented sample and a free powder of NdCo$_4$Al at room temperature.

Fig. 2. (Color online) Temperature dependence of magnetization of the magnetic-field-aligned NdCo$_4$Al alloy with H∥and⊥c axis, respectively.

homogeneity the sample was annealed at 1173 K for a week in an evacuated quartz tube. Magnetic-field-aligned NdCo$_4$Al alloy was prepared at 350 K by solidifying the mixture of epoxy resin and the powder specimen (≦40 μm) in a magnetic field of 5 kOe. At 350 K, the easy magnetization axis of NdCo$_4$Al alloy was c axis [15–19] and the magnetic moments would arrange along that direction. The hexagonal CaCu$_5$-type structure (*P6/mmm* space group) for polycrystalline NdCo$_4$Al Alloy was confirmed by X-ray powder diffraction (XRD) analysis at room temperature with Cu Kα radiation. Magnetic measurements were carried out using a vibrating sample magnetometer (7407, Lakeshore) under a magnetic field up to 10 kOe. Specific heat of NdCo$_4$Al polycrystalline alloy was investigated from 220 K to 360 K in physical property measurement system (6000, Quantum Design).

3. Results and discussion

To characterize the preferred orientation of magnetic-field-aligned alloy, a transverse section of the sample with the direction perpendicular to the magnetic field is cut for XRD measurement. For comparison, the XRD pattern for the polycrystalline powder is also presented. As shown in Fig. 1(b), the powder sample displays a random crystallographic orientation and all the peaks can be indexed as the hexagonal CaCu$_5$-type structure. In the case of magnetic-field-aligned alloy, many diffraction peaks are remarkably suppressed and only two greatly enhanced (001) and (002) peaks can be observed, indicating that the sample is orientated along c axis by a magnetic-field-aligned technology.

Temperature dependence of magnetization (M–T curve) for the magnetic-field-aligned NdCo$_4$Al alloy is measured from 220 K to 360 K with a magnetic field of 2 kOe parallel and perpendicular to c axis, respectively. In the low temperature, the MCA of Nd sublattice is larger than that of Co sublattice, and consequently, the total magnetic moment lies in the ab plane. When the axial MCA of Co sublattice is dominant, the c axis becomes the easy magnetization direction. Due to
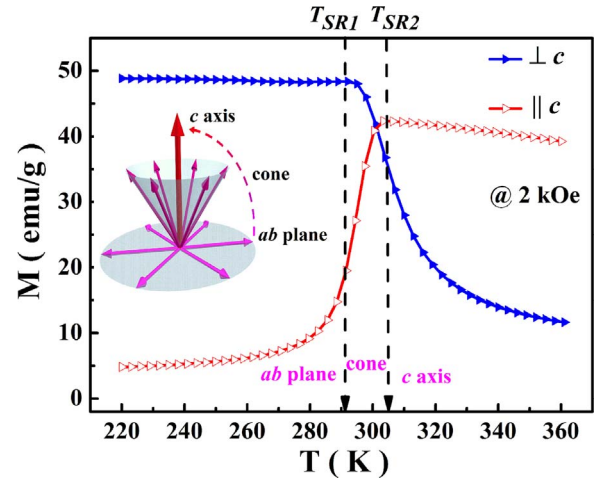
the strong competition between these two MCAs, the conical arrangement of magnetic moment which is between the ab plane and the c axis is produced. As a result, the arrangement of magnetic moment would undergo plane-cone and cone-axis SR transitions, which occur around T_{SR1} and T_{SR2}, respectively. As shown in Fig. 2, upon partial substitution of Al for Co, T_{SR1} and T_{SR2} of NdCo$_4$Al alloy are 293 K and 305 K, which are larger than these of NdCo$_5$ single crystal, respectively [2]. It is worth noting that the magnetization mainly increases or decreases with the increase of temperature, for the magnetic field parallel and perpendicular to c axis, respectively. The different M–T behavior for NdCo$_4$Al alloy is attributed to the change of MCA with the variation of temperature and meaningful for achieving enhanced rotating MCE, which will be discussed later.

Fig. 3(a) and (b) present magnetic field dependence of magnetization for NdCo$_4$Al alloy at 270 K and 360 K, respectively. At 270 K, the magnetization tends to be saturated at 5 kOe with the magnetic field perpendicular to c axis and the saturation magnetization is 62 emu/g. However, for the magnetic field parallel to c axis, the magnetization curve does not show a tendency of saturation even at 10 kOe, revealing the characteristic of hard magnetization axis. On the contrary, at 360 K, the magnetization tends to be saturated at 2 kOe with the magnetic field parallel to c axis and the saturation magnetization is 57 emu/g, suggesting that the easy magnetization axis has changed from ab plane to c axis above T_{SR2}. As a result, a hard magnetization behavior is observed when the magnetic field is perpendicular to c axis, which is shown in Fig. 3(b). Angle dependence of magnetization curves are measured by rotating the magnetic-field-aligned NdCo$_4$Al alloy from parallel to perpendicular to c axis under a magnetic field of 2 kOe. Here, θ is defined as the angle between the magnetic-field-aligned direction (c axis) and the applied magnetic field direction. As shown in the insets of Fig. 3(a) and (b), the magnetization decreases or increases gradually by rotating the sample from 0° to 90°, respectively, suggesting that the rotating MCE can be detected in this magnetic-field-aligned polycrystalline alloy.

A series of selected isothermal curves for NdCo$_4$Al alloy are measured from 220 K to 360 K with the magnetic field parallel and perpendicular to c axis, which are shown in Fig. 3(c) and (d), respectively. In the case of parallel direction, the magnetization first increases monotonously with increasing temperature until 300 K since the easy magnetization direction gradually changes from ab plane to c axis. However, when the temperature is higher than T_{SR2}, c axis becomes the easy magnetization axis, and then the magnetization decreases with increasing temperature [15], which leads to some crossovers in isothermal magnetization curves. As the magnetic field is perpendicular to c axis, the magnetization decreases monotonously