https://doi.org/10.1016/j.jnoncrysol.2021.121076

Magnetocaloric effect and magnetostriction of a binary $Nd_{50}Co_{50}$ metallic glass

Q. Wang[1], B. Z. Tang[1], K. C. Chan[2], M. B. Tang[3], D. Ding[1], and L. Xia[1,*]

[1] Institute of Materials, Shanghai University, Shanghai 200072, China

[2] Department of Industrial and Systems Engineering, The Hong Kong Polytechnic University, Hung Hom, Hong Kong

[3]Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai 200050, China

Abstract

The formability and magnetic properties of a low cost $Nd_{50}Co_{50}$ binary metallic glass were studied in the present work. The $Nd_{50}Co_{50}$ binary alloy was successfully vitrified into amorphous state with a poor but sufficient formability for glassy ribbon. The $Nd_{50}Co_{50}$ glassy sample exhibits a spin-glass-like behavior with a Curie temperature of ~ 78 K and a spin freezing temperature of ~ 61 K. The magnetocaloric properties of the $Nd_{50}Co_{50}$ glassy sample were poor and the mechanism involved was studied. The magnetostriction of the $Nd_{50}Co_{50}$ glassy sample under 5 T reached to 170 ppm at 30 K, which is not as high as those of Tb(Dy)-based amorphous alloys but much higher than those of TM-based metallic glasses. The binary $Nd_{50}Co_{50}$ alloy is expected to play a role as basic alloy for developing low-cost multicomponent metallic glasses with outstanding glass formability and magnetostriction.

Keywords: metallic glass, spin glass, magnetic entropy change, magnetostriction

---

* Corresponding authors. Email: xialei@shu.edu.cn (L. Xia)

1. Introduction

Metallic glasses composed of rare earth (RE) metals and transition metals (TM) exhibit very attractive properties due to their disordered atomic configuration lacking of long range order [1-3]. For example, the critical section thickness of Gd-TM-based metallic glasses reaches to several millimeters [4,5]. These amorphous Gd-TM-based alloys exhibit extraordinary magnetocaloric properties, such as ultra-large refrigeration capacity (usually several times larger than those of the intermetallic compounds) and large maximum magnetic entropy change ($-\Delta S_m^{peak}$, comparable or even superior to that of the pure Gd) at low temperature [4-9]. Besides, in contrast to the intermetallic compounds, the tunable Curie temperature of these Gd-based amorphous alloys via compositional adjustment is essential for the fabrication of amorphous composites with flattened magnetic entropy change curve [8,9], which is required for these amorphous composites to be used as magnetic refrigerants in an Ericsson cycle. More recently, the discovery of excellent magnetoelastic properties in the amorphous Tb(Dy)-TM alloys provides a new way for the development of novel magnetostriction material to overcome the shortages of traditional magnetostriction materials [10-12], such as brittleness, poor corrosion resistance, high energy loss due to the high coercivity and low electric resistance. These glassy Tb(Dy)-TM magnetostriction materials with excellent magnetoelastic properties have received more and more attentions because they are promising candidates for the key component of sensors, sonar, actuators and energy collector.

Unfortunately, the major component of these two kinds of metallic glasses, that is, the heavy RE elements Gd, Tb and Dy, are so expensive that they are hard to be applied extensively. The light RE (LRE) elements, such as Nd and Pr, are much cheaper than the heavy RE elements. In addition, the Nd(Pr)-TM-based alloys are good glass former and can be easily fabricated into bulk amorphous samples [13-15]. Therefore, to achieve good magnetocaloric properties or magnetoelastic properties in the Nd(Pr)-TM-based glassy alloys is of significant importance for the industrial application of these metallic glasses.

Binary amorphous alloys play a simple but important role as the basic alloys to develop multicomponent glass forming alloys with a combination of improved formability and enhanced physical properties. In this work, a binary $Nd_{50}Co_{50}$ alloy was employed for the investigation of the formability, magnetic properties, magnetocaloric effect and magnetostriction of its glassy sample. The sample was vitrified into ribbon with ~1 millimeter in width and ~ 40 micrometers in thickness. Glass formability of the $Nd_{50}Co_{50}$ alloy was evaluated from the thermal properties of its glassy. Magnetic properties of the glassy sample were measured systematically so as to obtain the Curie temperature (T_c), spin freezing temperature (T_f), saturation magnetization (M_s), $-\Delta S_m$ curve and magnetostriction (λ) of the $Nd_{50}Co_{50}$ amorphous alloy.

2. Experimental procedures

Nd and Co pure metals purchased from the Trillion Metals Co., Ltd. with a purity of above 99.9% (at%) were mixed together according to the nominal $Nd_{50}Co_{50}$ composition and then arc-melted by a non-consumable electrode for several times in a high vacuum arc furnace to prepared the mother alloy ingot. The ingot was broken into pieces and remelted in a quartz tube under the protection of an Ar atmosphere, and then sprayed to a rotating copper wheel to obtain the $Nd_{50}Co_{50}$ ribbons.

A Rigaku D\max-rC diffractometer was applied to ensure the amorphous structure of the melt-spun ribbons.

Differential scanning calorimetry (DSC) measurement of the amorphous ribbon was performed on a DIAMOND calorimeter (Perkin-Elmer) at a heating rate of 0.667 K/s so as to obtain the onset temperature of glass transition (T_g) and crystallization (T_x). The liquidus temperature (T_l) of the $Nd_{50}Co_{50}$ binary alloy obtained from the Nd-Co equilibrium phase diagram is ~ 1110 K [16].

A vibrating sample magnetometer, as one of the testing modules of a Quantum Design Physical Properties Measurement System (PPMS, model 6000), was used to measure the magnetization-temperature (M-T) curve, hysteresis loops and magnetization (M-H) curves of the amorphous ribbon. Magnetostriction of the $Nd_{50}Co_{50}$ glassy sample was also measured in PPMS by a KYOWA KFL-02-120-C1 foil strain gauge calibrated by pure aluminum.

3. Results and discussion

The vitrification of the binary $Nd_{50}Co_{50}$ alloy was ascertained by the smooth diffraction hump and the absence of sharp crystalline peaks in the X-ray diffraction pattern, as shown in Figure 1. A weak endothermic glass transition hump and a sharp crystallization peak, as shown in the inset of Fig. 1, were found in the continuous DSC trace of the glassy ribbon. T_g and T_x of the $Nd_{50}Co_{50}$ ribbon are about 415 K and 472 K, respectively. The reduced glass transition temperature (T_{rg}= 0.374) [17] and the parameter γ (=0.31) [18] indicate the poor formability of the $Nd_{50}Co_{50}$ alloy. The critical section thickness (Z_c, defined as $2.8\times10^{-7}\exp(41.7\gamma)$) [18] of the ribbon is about 113 micrometers, which is sufficient for the binary $Nd_{50}Co_{50}$ alloy to be quenched into glassy ribbons.

After cooling from room temperature to 10 K without a magnetic field, we measured the zero-field-cool (ZFC) M-T curve of the $Nd_{50}Co_{50}$ glassy ribbon when heating the sample from 10 K to 300 K under 0.03 T. Then we cooled the sample from 300 K to 10 K under 0.03 T and measure the field-cool (FC) M-T curve of the sample when heating the sample from 10 K to 300 K under 0.03 T. Figure 2 (a) shows the difference between the two M-T curves: they are almost the same at temperatures above 60 K, but diverge from 60 K to low temperatures. The λ-shaped M-T curves indicate the possible spin-glass-like behavior in the $Nd_{50}Co_{50}$ glassy sample [19-21]. From the M-T curves, T_c and T_f of the glassy sample can be obtained to be ~ 88 K and 61 K, respectively.

The spin-glass-like behavior can also be ascertained by the magnetization behaviors of the $Nd_{50}Co_{50}$ glassy sample. As is known, the spin-glass behaviors in the RE-TM-based metallic glasses are closely related to the random magnetic anisotropy, which is induced by the local random electrostatic field and act as the leading factor influencing the magnetization behaviors of the amorphous alloys at temperatures well below T_f. Therefore, these amorphous alloys are expected to be hard magnetic at temperatures much lower than their T_f because of the broken rotational symmetry of the Hamiltonian by the random magnetic anisotropy [11,22,23]. Figure 2 (b) shows the hysteresis loops of the $Nd_{50}Co_{50}$ glass sample at 10 K, 70 K and 150 K. As expected, the sample is hard magnetic with a coercivity of ~ 0.66 T with a M_s of about 64 Am^2/kg at 10 K (well below T_f). At 150 K (well above T_c), the sample shows paramagnetic behavior. At 70 K, which is between the T_c and T_f, the sample exhibits soft magnetic behavior because the magnetization behavior of the glassy sample is dominated by the exchange interaction between Nd and Co.

Figure 3 (a) shows the magnetization curves of the $Nd_{50}Co_{50}$ glassy ribbon measured at various temperatures between 10 K and 150 K under a field of 5 T. The magnetization under a field less than 0.1 T decreases from 50 K to 10 K, which also illustrates the effect of spin-glass-like behavior on the magnetization of the sample. On the other hand, we can also obtain the ($-\Delta S_m$)-temperature curves under various magnetic fields from these magnetization curves, as shown in Figure 3 (b). The $-\Delta S_m$ of the $Nd_{50}Co_{50}$ ribbon is irreversible at temperatures much lower than T_f, and even decreases to below zero at 20 K, similar to that of other RE-TM metallic glasses that exhibit spin-glass-like behaviors [19-21]. The maximum $-\Delta S_m$ ($-\Delta S_m^{peak}$) for the $Nd_{50}Co_{50}$ glassy sample is only 4.15 J K^{-1} kg^{-1} even under a high magnetic field of 5 T, which much lower than that of Gd-based, Tb-based and Dy-based amorphous alloys [3-10,19-21]. The poor magnetocaloric properties of the $Nd_{50}Co_{50}$ metallic glass may be resulted from two factors: the weak interaction between Nd and Co atoms due to the low effective magnetic moment of Nd atoms [24].

Although the magnetocaloric properties of the $Nd_{50}Co_{50}$ metallic glass are very poor, its high coercivity indicates that the magnetoelastic performance of the sample may be not so bad because both the hysteresis and the magnetostriction are closely related to the random magnetic anisotropy of the glassy alloy. Figure 4 shows the magnetostriction of the $Nd_{50}Co_{50}$ glassy sample under the field of $0 \rightarrow 5$ T at temperatures below T_f. The λ of the sample increases monotonically from 60 K to 30 K and reaches to a maximum at 30 K with λ = 119 ppm under 1.5 T and λ = 174 ppm under 5 T. Although the λ of the $Nd_{50}Co_{50}$ glassy sample is not as high as those of the Tb(Dy)-based metallic glasses [10-12], it is still much larger than those of TM-based glassy alloys [25-27]. Considering that the Nd-based metallic glasses are much lower cost than the Tb(Dy)-based amorphous alloys, the $Nd_{50}Co_{50}$ glassy alloy with a medium λ value is still a better choice for the industrial applications of magnetoelastic materials. Besides, the binary $Nd_{50}Co_{50}$ alloy can act as a basic alloy for developing ternary or multicomponent metallic glasses with outstanding glass formability and magnetostriction.

4. **Conclusions**

A low cost $Nd_{50}Co_{50}$ binary alloy was successfully vitrified into amorphous state in the shape of ribbon in this work. The T_{rg}, γ and Z_c of the glassy ribbon indicates that the glass formability of the binary alloy is poor, but is sufficient for it to be vitrified into glassy ribbons. The magnetic, magnetocaloric and magnetoelastic properties of the glassy ribbon were investigated. The binary metallic glass shows a spin-glass-like behavior with a T_c of ~ 88 K and a T_f of ~ 61 K. Hysteresis loops of the amorphous ribbon indicate that the sample is paramagnetic well above the T_c, soft magnetic within the T_c and T_f, and hard magnetic well below T_f. The spin-glass-like behavior of the sample can also be ascertained by the decreasing magnetization from 50 K to 10 K under a field less than 0.1 T. $-\Delta S_m^{peak}$ of the $Nd_{50}Co_{50}$ glassy sample is much lower than those of other RE-based amorphous alloys. The lower $-\Delta S_m^{peak}$ of the $Nd_{50}Co_{50}$ sample is supposed to be mainly resulted from the weak magnetic interaction between Nd and Co atoms due to the low effective magnetic moment of Nd atoms. λ of the sample increases from 60 K to 30 K and reaches to a maximum (λ = 119 ppm under 1.5 T and λ = 174 ppm under 5 T) at 30 K. Although the λ of the $Nd_{50}Co_{50}$ glassy sample is not as high as those of the Tb(Dy)-based metallic glasses, it is still much larger than those of TM-based glassy alloys. Considering its low cost and simple composition, the binary $Nd_{50}Co_{50}$ metallic glass can play a mother alloy role for developing economical multicomponent magnetoelastic metallic glasses.

Acknowledgements

The work described in this paper was supported by the National Natural Science Foundation of China (Grant Nos. 51671119, 51871139 and 52071196), and by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. PolyU 15253916).

References

[1] C. Suryanarayana, A. Inoue, Bulk Metallic Glasses, CRC Press, 2011.

[2] H. S. Chen, Glassy metals, Rep. Prog. Phys. 43 (1980) 353-432.

[3] Q. Luo, W.H. Wang, Rare earth based bulk metallic glasses, J. Non-Cryst. Solids 355 (2009) 759-775.

[4] D. Ding, P. Wang, Q. Guan, M.B. Tang, L. Xia, Excellent Glass Forming Ability and Refrigeration Capacity of a $Gd_{55}Al_{20}Ni_{12}Co_{10}Mn_3$ Bulk Metallic Glass, Chin. Phys. Lett. 30 (2013) 096104.

[5] C. Wu, D. Ding, L. Xia, Effect of Al Addition on the Glass-Forming Ability and Magnetic Properties of a Gd-Co Binary Amorphous Alloy. Chin. Phys. Lett. 33 (2016) 016102.

[6] Z.G. Zheng, X.C. Zhong, K.P. Su, H.Y. Yu, Z.W. Liu, D.C. Zeng, Magnetic properties and large magnetocaloric effects in amorphous Gd-Al-Fe alloys for magnetic refrigeration, Sci. China Phys. Mech. Astron. 54 (2011) 1267-1270.

[7] Q. Luo, D. Q. Zhao, M.X. Pan, W.H. Wang, Magnetocaloric effect in Gd-based bulk metallic glasses, Appl. Phys. Lett. 89 (2006) 081914.

[8] L.Y. Ma, L.H. Gan, K.C. Chan, D. Ding, L. Xia, Achieving a table-like magnetic entropy change across the ice point of water with tailorable temperature range in Gd-Co-based amorphous hybrids, J. Alloys Compd. 723 (2017) 197-200.

[9] C. Wu, D. Ding, L. Xia, K.C. Chan, Achieving tailorable magneto-caloric effect in the Gd-Co binary amorphous alloys, AIP Adv. 6 (2016) 035302.

[10] B.Z. Tang, D.Q. Guo, L. Xia, D. Ding, K.C. Chan, Magnetoelastic and magnetocaloric properties of $Tb_{62.5}Co_{37.5}$ amorphous alloy, J. Alloys Compd. 728 (2017) 747-751.

[11] T. Speliotis, D. Niarchos, Extraordinary magnetization of amorphous TbDyFe films, Microelectron. Eng. 112 (2013) 183-187.

[12] L. Xia, K.C. Chan, L. Zhao, D. Ding, B.Z. Tang, Magnetic properties and magnetostriction of a binary $Dy_{50}Co_{50}$ amorphous alloy, J. Non-Cryst. Solids 493

(2018) 29-32.

[13] A. Inoue, T. Zhang, W. Zhang, A. Takeuchi, Bulk Nd-Fe-Al amorphous alloys with hard magnetic properties, Mater. T. JIM 37 (1996) 99-108.

[14] A. Inoue, T. Zhang, A. Takeuchi, Preparation of bulk Pr-Fe-Al amorphous alloys and characterization of their hard magnetic properties, Mater. T. JIM 37 (1996) 1731-1740.

[15] L. Xia, S.S. Fang, C.L. Jo, Y.D. Dong, Glass forming ability and microstructure of hard magnetic $Nd_{60}Al_{20}Fe_{20}$ glass forming alloy, Intermetallics 14 (2006) 1098-1101.

[16] A. Hussain, M.A. Van Ende, J. Kim, I.H. Jung, Critical thermodynamic evaluation and optimization of the Co-Nd, Cu-Nd and Nd-Ni systems, CALPHAD 41 (2013) 26-41.

[17] D. Turnbull, Under what conditions can a glass be formed? Contemp. Phys. 10 (1969) 473-488.

[18] Z. Lu, C. Liu, Glass formation criterion for various glass-forming systems, Phys. Rev. Lett. 91 (2003) 115505.

[19] F. Yuan, J. Du, B.L. Shen, Controllable spin-glass behavior and large magnetocaloric effect in Gd-Ni-Al bulk metallic glasses, Appl. Phys. Lett. 101 (2012) 032405.

[20] Q. Luo, B. Schwarz, N. Mattern, J. Eckert, Giant irreversible positive to large reversible negative magnetic entropy change evolution in Tb-based bulk metallic glass, Phys. Rev. B 82 (2010) 024204.

[21] Q. Luo, B. Schwarz, N. Mattern, J. Eckert, Irreversible and reversible magnetic entropy change in a Dy-based bulk metallic glass, Intermetallics 30 (2012) 76-79.

[22] C. Jayaprakash, S. Kirkpatrick, Random anisotropy models in the Ising limit, Phys.
Rev. B 21 (1980) 4072.

[23] R. Harris, M. Plischke, M.J. Zuckermann, New model for amorphous magnetism, Phys. Rev. Lett. 31 (1974) 160.

[24] R.Y. Fang, D.S. Dai, Z.X. Lui, H. Wang, Y.P. Ji, Low temperature magnetic properties of Nd_xCo_{1-x} amorphous thin films, J. Magn. Magn. Mater. 58 (1986) 273-279.

[25] Q.A. Abbas, N.A. Morley, Fabrication and characterization of magnetostrictive amorphous FeGaSiB thin films, J. Magn. Magn. Mater. 439 (2017) 353-357.

[26] S. Gudoshnikov, A. Ignatov, V. Tarasov, S. Gorbunov, V. Molokanov, T. Chueva, N. Usov, Magnetoelastic properties of Co-based amorphous ferromagnetic microwires, Phys. Status Silidi A 213 (2016) 368-371.

[27] V. Rodioniva, I. Baraban, K. Chichay, A. Litvinova, N. Perov, The stress components effect on the Fe-based microwires magnetostatic and magnetostrictive properties, J. Magn. Magn. Mater. 422 (2017) 216-220.

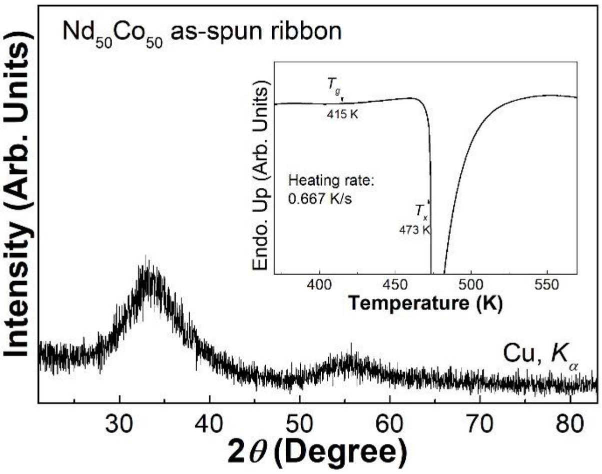
Figure captions

Figure 1 XRD pattern of the $Nd_{50}Co_{50}$ as-spun ribbon, the inset is the DSC curve of the ribbon at a heating rate of 0.667 K/s.

Figure 2 (a) FC and ZFC *M*-*T* curves of the $Nd_{50}Co_{50}$ amorphous ribbon measured in the heating process under a magnetic field of 0.03 T; (b) The hysteresis loops of the amorphous ribbon measured at 10 K, 70 K and 150 K.

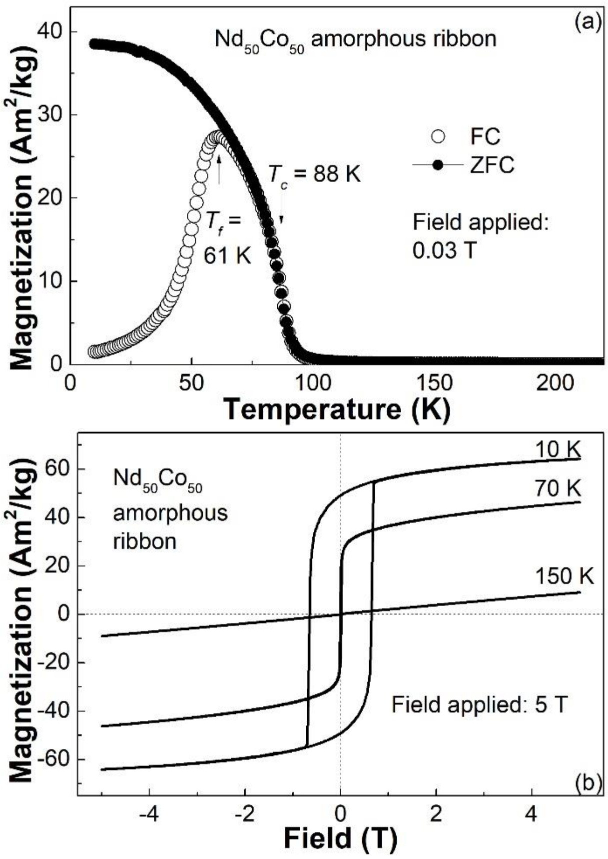
Figure 3 (a) The isothermal *M*-*H* curves of the $Nd_{50}Co_{50}$ amorphous ribbon measured at various temperatures under a magnetic field of 5 T; (b) The $(-\Delta S_m)$-T curves of the $Nd_{50}Co_{50}$ amorphous ribbon under different magnetic fields.

Figure 4 The magnetostriction curves of the $Nd_{50}Co_{50}$ amorphous ribbon measured at the temperature of 30 K, 40 K, 50 K and 60 K under a field of 5 T.



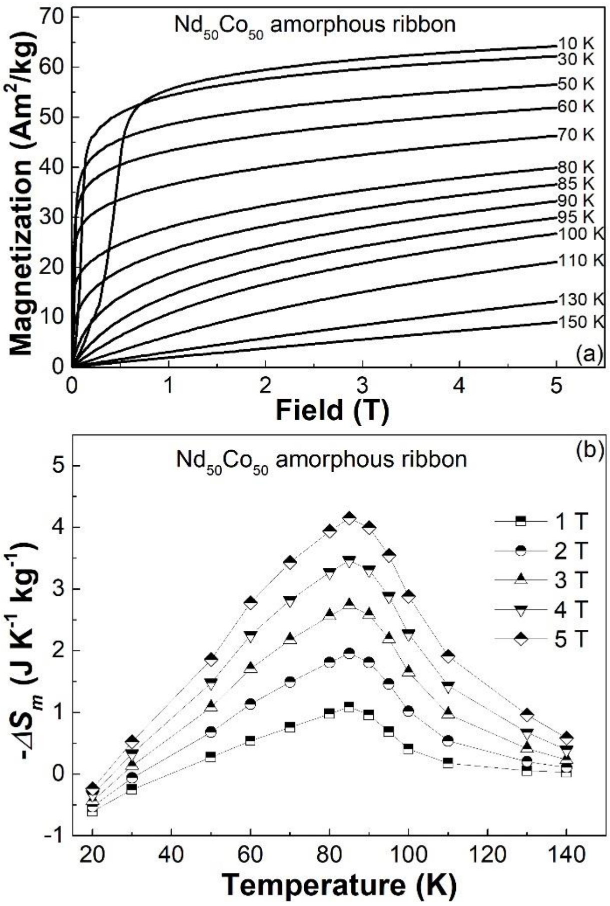
Q. Wang *et al*.

Figure 1



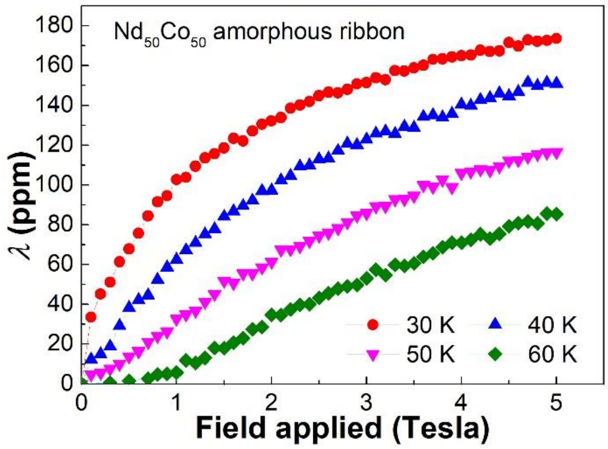
Q. Wang *et al*.

Figure 2



Q. Wang *et al*.

Figure 3



Q. Wang *et al*.

Figure 4

Magnetocaloric effect and magnetostriction of a binary $Nd_{50}Co_{50}$ metallic glass

Q. Wang[1], B. Z. Tang[1], K. C. Chan[2], M. B. Tang[3], D. Ding[1], and L. Xia[1,*]

[1] Institute of Materials, Shanghai University, Shanghai 200072, China

[2] Department of Industrial and Systems Engineering, The Hong Kong Polytechnic University, Hung Hom, Hong Kong

[3]Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai 200050, China

Abstract

The formability and magnetic properties of a low cost $Nd_{50}Co_{50}$ binary metallic glass were studied in the present work. The $Nd_{50}Co_{50}$ binary alloy was successfully vitrified into amorphous state with a poor but sufficient formability for glassy ribbon. The $Nd_{50}Co_{50}$ glassy sample exhibits a spin-glass-like behavior with a Curie temperature of ~ 78 K and a spin freezing temperature of ~ 61 K. The magnetocaloric properties of the $Nd_{50}Co_{50}$ glassy sample were poor and the mechanism involved was studied. The magnetostriction of the $Nd_{50}Co_{50}$ glassy sample under 5 T reached to 170 ppm at 30 K, which is not as high as those of Tb(Dy)-based amorphous alloys but much higher than those of TM-based metallic glasses. The binary $Nd_{50}Co_{50}$ alloy is expected to play a role as basic alloy for developing low-cost multicomponent metallic glasses with outstanding glass formability and magnetostriction.

Keywords: metallic glass, spin glass, magnetic entropy change, magnetostriction

* Corresponding authors. Email: xialei@shu.edu.cn (L. Xia)

1. Introduction

Metallic glasses composed of rare earth (RE) metals and transition metals (TM) exhibit very attractive properties due to their disordered atomic configuration lacking of long range order [1-3]. For example, the critical section thickness of Gd-TM-based metallic glasses reaches to several millimeters [4,5]. These amorphous Gd-TM-based alloys exhibit extraordinary magnetocaloric properties, such as ultra-large refrigeration capacity (usually several times larger than those of the intermetallic compounds) and large maximum magnetic entropy change ($-\Delta S_m^{peak}$, comparable or even superior to that of the pure Gd) at low temperature [4-9]. Besides, in contrast to the intermetallic compounds, the tunable Curie temperature of these Gd-based amorphous alloys via compositional adjustment is essential for the fabrication of amorphous composites with flattened magnetic entropy change curve [8,9], which is required for these amorphous composites to be used as magnetic refrigerants in an Ericsson cycle. More recently, the discovery of excellent magnetoelastic properties in the amorphous Tb(Dy)-TM alloys provides a new way for the development of novel magnetostriction material to overcome the shortages of traditional magnetostriction materials [10-12], such as brittleness, poor corrosion resistance, high energy loss due to the high coercivity and low electric resistance. These glassy Tb(Dy)-TM magnetostriction materials with excellent magnetoelastic properties have received more and more attentions because they are promising candidates for the key component of sensors, sonar, actuators and energy collector.

Unfortunately, the major component of these two kinds of metallic glasses, that is, the heavy RE elements Gd, Tb and Dy, are so expensive that they are hard to be applied extensively. The light RE (LRE) elements, such as Nd and Pr, are much cheaper than the heavy RE elements. In addition, the Nd(Pr)-TM-based alloys are good glass former and can be easily fabricated into bulk amorphous samples [13-15]. Therefore, to achieve good magnetocaloric properties or magnetoelastic properties in the Nd(Pr)-TM-based glassy alloys is of significant importance for the industrial application of these metallic glasses.

Binary amorphous alloys play a simple but important role as the basic alloys to develop multicomponent glass forming alloys with a combination of improved formability and enhanced physical properties. In this work, a binary $Nd_{50}Co_{50}$ alloy was employed for the investigation of the formability, magnetic properties, magnetocaloric effect and magnetostriction of its glassy sample. The sample was vitrified into ribbon with ~1 millimeter in width and ~ 40 micrometers in thickness. Glass formability of the $Nd_{50}Co_{50}$ alloy was evaluated from the thermal properties of its glassy. Magnetic properties of the glassy sample were measured systematically so as to obtain the Curie temperature (T_c), spin freezing temperature (T_f), saturation magnetization (M_s), $-\Delta S_m$ curve and magnetostriction (λ) of the $Nd_{50}Co_{50}$ amorphous alloy.

2. Experimental procedures

Nd and Co pure metals purchased from the Trillion Metals Co., Ltd. with a purity of above 99.9% (at%) were mixed together according to the nominal $Nd_{50}Co_{50}$ composition and then arc-melted by a non-consumable electrode for several times in a high vacuum arc furnace to prepare the mother alloy ingot. The ingot was broken into pieces and remelted in a quartz tube under the protection of an Ar atmosphere, and then sprayed to a rotating copper wheel to obtain the $Nd_{50}Co_{50}$ ribbons.

A Rigaku D\max-rC diffractometer was applied to ensure the amorphous structure of the melt-spun ribbons.

Differential scanning calorimetry (DSC) measurement of the amorphous ribbon was performed on a DIAMOND calorimeter (Perkin-Elmer) at a heating rate of 0.667 K/s so as to obtain the onset temperature of glass transition (T_g) and crystallization (T_x). The liquidus temperature (T_l) of the $Nd_{50}Co_{50}$ binary alloy obtained from the Nd-Co equilibrium phase diagram is ~ 1110 K [16].

A vibrating sample magnetometer, as one of the testing modules of a Quantum Design Physical Properties Measurement System (PPMS, model 6000), was used to measure the magnetization-temperature (M-T) curve, hysteresis loops and magnetization (M-H) curves of the amorphous ribbon. The error limit of the magnetization is less than 0.02 Am^2/kg. Magnetostriction of the $Nd_{50}Co_{50}$ glassy sample was also measured in PPMS by a KYOWA KFL-02-120-C1 foil strain gauge calibrated by pure aluminum.

3. Results and discussion

The vitrification of the binary $Nd_{50}Co_{50}$ alloy was ascertained by the smooth diffraction hump and the absence of sharp crystalline peaks in the X-ray diffraction pattern, as shown in Figure 1. A weak endothermic glass transition hump and a sharp crystallization peak, as shown in the inset of Fig. 1, were found in the continuous DSC trace of the glassy ribbon. T_g and T_x of the $Nd_{50}Co_{50}$ ribbon are about 415 K and 472 K, respectively. The reduced glass transition temperature (T_{rg}= 0.374) [17] and the parameter γ (=0.31) [18] indicate the poor formability of the $Nd_{50}Co_{50}$ alloy. The critical section thickness (Z_c, defined as $2.8\times10^{-7}\exp(41.7\gamma)$) [18] of the ribbon is about 113 micrometers, which is sufficient for the binary $Nd_{50}Co_{50}$ alloy to be quenched into glassy ribbons.

After cooling from room temperature to 10 K without a magnetic field, we measured the zero-field-cool (ZFC) M-T curve of the $Nd_{50}Co_{50}$ glassy ribbon when heating the sample from 10 K to 300 K under 0.03 T. Then we cooled the sample from 300 K to 10 K under 0.03 T and measured the field-cool (FC) M-T curve of the sample when heating the sample from 10 K to 300 K under 0.03 T. Figure 2 (a) shows the difference between the two M-T curves: they are almost the same at temperatures above 60 K, but diverge from 60 K to low temperatures. The λ-shaped M-T curves indicate the possible spin-glass-like behavior in the $Nd_{50}Co_{50}$ glassy sample [19-21]. From the M-T curves, T_c and T_f of the glassy sample can be obtained to be ~ 88 K and 61 K, respectively.

The spin-glass-like behavior can also be ascertained by the magnetization behaviors of the $Nd_{50}Co_{50}$ glassy sample. As is known, the spin-glass behaviors in the RE-TM-based metallic glasses are closely related to the random magnetic anisotropy, which is induced by the local random electrostatic field and acts as the leading factor influencing the magnetization behaviors of the amorphous alloys at temperatures well below T_f. Therefore, these amorphous alloys are expected to be hard magnetic at temperatures much lower than their T_f because of the broken rotational symmetry of the Hamiltonian by the random magnetic anisotropy [11,22,23]. Figure 2 (b) shows the hysteresis loops of the $Nd_{50}Co_{50}$ glass sample at 10 K, 70 K and 150 K. As expected, the sample is hard magnetic with a coercivity of ~ 0.66 T with a M_s of about 64 Am^2/kg at 10 K (well below T_f). At 150 K (well above T_c), the sample shows paramagnetic behavior. At 70 K, which is between the T_c and T_f, the sample exhibits soft magnetic behavior because the magnetization behavior of the glassy sample is dominated by the exchange interaction between Nd and Co.

Figure 3 (a) shows the magnetization curves of the $Nd_{50}Co_{50}$ glassy ribbon measured at various temperatures between 10 K and 150 K under a field of 5 T. The magnetization under a field less than 0.1 T decreases from 50 K to 10 K, which also illustrates the effect of spin-glass-like behavior on the magnetization of the sample. On the other hand, we can also obtain the ($-\Delta S_m$)-temperature curves under various magnetic fields from these magnetization curves, as shown in Figure 3 (b). The $-\Delta S_m$ of the $Nd_{50}Co_{50}$ ribbon is irreversible at temperatures much lower than T_f, and even decreases to below zero at 20 K, similar to that of other RE-TM metallic glasses that exhibit spin-glass-like behaviors [19-21]. The maximum $-\Delta S_m$ ($-\Delta S_m^{peak}$) for the $Nd_{50}Co_{50}$ glassy sample is only 4.15 J K^{-1} kg^{-1} even under a high magnetic field of 5 T, which much lower than that of Gd-based, Tb-based and Dy-based amorphous alloys [3-10,19-21]. The poor magnetocaloric properties of the $Nd_{50}Co_{50}$ metallic glass may be resulted from two factors: the weak interaction between Nd and Co atoms due to the low effective magnetic moment of Nd atoms [24].

Although the magnetocaloric properties of the $Nd_{50}Co_{50}$ metallic glass are very poor, its high coercivity indicates that the magnetoelastic performance of the sample may be not so bad because both the hysteresis and the magnetostriction are closely related to the random magnetic anisotropy of the glassy alloy. Figure 4 shows the magnetostriction of the $Nd_{50}Co_{50}$ glassy sample under the field of 0 → 5 T at temperatures below T_f. The λ of the sample increases monotonically from 60 K to 30 K and reaches to a maximum at 30 K with λ = 119 ppm under 1.5 T and λ = 174 ppm under 5 T. Although the λ of the $Nd_{50}Co_{50}$ glassy sample is not as high as those of the Tb(Dy)-based metallic glasses [10-12], it is still much larger than those of TM-based glassy alloys [25-27]. Considering that the Nd-based metallic glasses are much lower cost than the Tb(Dy)-based amorphous alloys, the $Nd_{50}Co_{50}$ glassy alloy with a medium λ value is still a better choice for the industrial applications of magnetoelastic materials. Besides, the binary $Nd_{50}Co_{50}$ alloy can act as a basic alloy for developing ternary or multicomponent metallic glasses with outstanding glass formability and magnetostriction.

4. Conclusions

A low cost $Nd_{50}Co_{50}$ binary alloy was successfully vitrified into amorphous state in the shape of ribbon in this work. The T_{rg}, γ and Z_c of the glassy ribbon indicate that the glass formability of the binary alloy is poor, but is sufficient for it to be vitrified into glassy ribbons. The magnetic, magnetocaloric and magnetoelastic properties of the glassy ribbon were investigated. The binary metallic glass shows a spin-glass-like behavior with a T_c of ~ 88 K and a T_f of ~ 61 K. Hysteresis loops of the amorphous ribbon indicate that the sample is paramagnetic well above the T_c, soft magnetic within the T_c and T_f, and hard magnetic well below T_f. The spin-glass-like behavior of the sample can also be ascertained by the decreasing magnetization from 50 K to 10 K under a field less than 0.1 T. $-\Delta S_m^{peak}$ of the $Nd_{50}Co_{50}$ glassy sample is much lower than those of other RE-based amorphous alloys. The lower $-\Delta S_m^{peak}$ of the $Nd_{50}Co_{50}$ sample is supposed to be mainly resulted from the weak magnetic interaction between Nd and Co atoms due to the low effective magnetic moment of Nd atoms. λ of the sample increases from 60 K to 30 K and reaches to a maximum (λ = 119 ppm under 1.5 T and λ = 174 ppm under 5 T) at 30 K. Although the λ of the $Nd_{50}Co_{50}$ glassy sample is not as high as those of the Tb(Dy)-based metallic glasses, it is still much larger than those of TM-based glassy alloys. Considering its low cost and simple composition, the binary $Nd_{50}Co_{50}$ metallic glass can play a mother alloy role for developing economical multicomponent magnetoelastic metallic glasses.

Acknowledgements

The work described in this paper was supported by the National Natural Science Foundation of China (Grant Nos. 51671119, 51871139 and 52071196), and by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. PolyU 15253916).

References

[1] C. Suryanarayana, A. Inoue, Bulk Metallic Glasses, CRC Press, 2011.

[2] H. S. Chen, Glassy metals, Rep. Prog. Phys. 43 (1980) 353-432.

[3] Q. Luo, W.H. Wang, Rare earth based bulk metallic glasses, J. Non-Cryst. Solids 355 (2009) 759-775.

[4] D. Ding, P. Wang, Q. Guan, M.B. Tang, L. Xia, Excellent Glass Forming Ability and Refrigeration Capacity of a $Gd_{55}Al_{20}Ni_{12}Co_{10}Mn_3$ Bulk Metallic Glass, Chin. Phys. Lett. 30 (2013) 096104.

[5] C. Wu, D. Ding, L. Xia, Effect of Al Addition on the Glass-Forming Ability and Magnetic Properties of a Gd-Co Binary Amorphous Alloy. Chin. Phys. Lett. 33 (2016) 016102.

[6] Z.G. Zheng, X.C. Zhong, K.P. Su, H.Y. Yu, Z.W. Liu, D.C. Zeng, Magnetic properties and large magnetocaloric effects in amorphous Gd-Al-Fe alloys for magnetic refrigeration, Sci. China Phys. Mech. Astron. 54 (2011) 1267-1270.

[7] Q. Luo, D. Q. Zhao, M.X. Pan, W.H. Wang, Magnetocaloric effect in Gd-based bulk metallic glasses, Appl. Phys. Lett. 89 (2006) 081914.

[8] L.Y. Ma, L.H. Gan, K.C. Chan, D. Ding, L. Xia, Achieving a table-like magnetic entropy change across the ice point of water with tailorable temperature range in Gd-Co-based amorphous hybrids, J. Alloys Compd. 723 (2017) 197-200.

[9] C. Wu, D. Ding, L. Xia, K.C. Chan, Achieving tailorable magneto-caloric effect in the Gd-Co binary amorphous alloys, AIP Adv. 6 (2016) 035302.

[10] B.Z. Tang, D.Q. Guo, L. Xia, D. Ding, K.C. Chan, Magnetoelastic and magnetocaloric properties of $Tb_{62.5}Co_{37.5}$ amorphous alloy, J. Alloys Compd. 728 (2017) 747-751.

[11] T. Speliotis, D. Niarchos, Extraordinary magnetization of amorphous TbDyFe films, Microelectron. Eng. 112 (2013) 183-187.

[12] L. Xia, K.C. Chan, L. Zhao, D. Ding, B.Z. Tang, Magnetic properties and magnetostriction of a binary $Dy_{50}Co_{50}$ amorphous alloy, J. Non-Cryst. Solids 493

(2018) 29-32.

[13] A. Inoue, T. Zhang, W. Zhang, A. Takeuchi, Bulk Nd-Fe-Al amorphous alloys with hard magnetic properties, Mater. T. JIM 37 (1996) 99-108.

[14] A. Inoue, T. Zhang, A. Takeuchi, Preparation of bulk Pr-Fe-Al amorphous alloys and characterization of their hard magnetic properties, Mater. T. JIM 37 (1996) 1731-1740.

[15] L. Xia, S.S. Fang, C.L. Jo, Y.D. Dong, Glass forming ability and microstructure of hard magnetic $Nd_{60}Al_{20}Fe_{20}$ glass forming alloy, Intermetallics 14 (2006) 1098-1101.

[16] A. Hussain, M.A. Van Ende, J. Kim, I.H. Jung, Critical thermodynamic evaluation and optimization of the Co-Nd, Cu-Nd and Nd-Ni systems, CALPHAD 41 (2013) 26-41.

[17] D. Turnbull, Under what conditions can a glass be formed? Contemp. Phys. 10 (1969) 473-488.

[18] Z. Lu, C. Liu, Glass formation criterion for various glass-forming systems, Phys. Rev. Lett. 91 (2003) 115505.

[19] F. Yuan, J. Du, B.L. Shen, Controllable spin-glass behavior and large magnetocaloric effect in Gd-Ni-Al bulk metallic glasses, Appl. Phys. Lett. 101 (2012) 032405.

[20] Q. Luo, B. Schwarz, N. Mattern, J. Eckert, Giant irreversible positive to large reversible negative magnetic entropy change evolution in Tb-based bulk metallic glass, Phys. Rev. B 82 (2010) 024204.

[21] Q. Luo, B. Schwarz, N. Mattern, J. Eckert, Irreversible and reversible magnetic entropy change in a Dy-based bulk metallic glass, Intermetallics 30 (2012) 76-79.

[22] C. Jayaprakash, S. Kirkpatrick, Random anisotropy models in the Ising limit, Phys.
Rev. B 21 (1980) 4072.

[23] R. Harris, M. Plischke, M.J. Zuckermann, New model for amorphous magnetism, Phys. Rev. Lett. 31 (1974) 160.

[24] R.Y. Fang, D.S. Dai, Z.X. Lui, H. Wang, Y.P. Ji, Low temperature magnetic properties of Nd_xCo_{1-x} amorphous thin films, J. Magn. Magn. Mater. 58 (1986) 273-279.

[25] Q.A. Abbas, N.A. Morley, Fabrication and characterization of magnetostrictive amorphous FeGaSiB thin films, J. Magn. Magn. Mater. 439 (2017) 353-357.

[26] S. Gudoshnikov, A. Ignatov, V. Tarasov, S. Gorbunov, V. Molokanov, T. Chueva, N. Usov, Magnetoelastic properties of Co-based amorphous ferromagnetic microwires, Phys. Status Silidi A 213 (2016) 368-371.

[27] V. Rodioniva, I. Baraban, K. Chichay, A. Litvinova, N. Perov, The stress components effect on the Fe-based microwires magnetostatic and magnetostrictive properties, J. Magn. Magn. Mater. 422 (2017) 216-220.

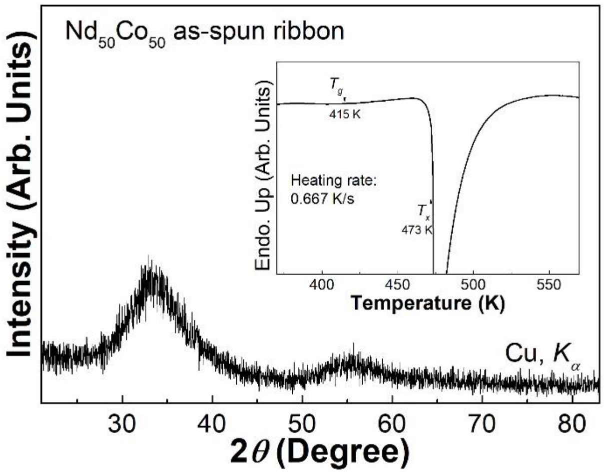
Figure captions

Figure 1 XRD pattern of the $Nd_{50}Co_{50}$ as-spun ribbon, the inset is the DSC curve of the ribbon at a heating rate of 0.667 K/s.

Figure 2 (a) FC and ZFC *M*-*T* curves of the $Nd_{50}Co_{50}$ amorphous ribbon measured in the heating process under a magnetic field of 0.03 T; (b) The hysteresis loops of the amorphous ribbon measured at 10 K, 70 K and 150 K.

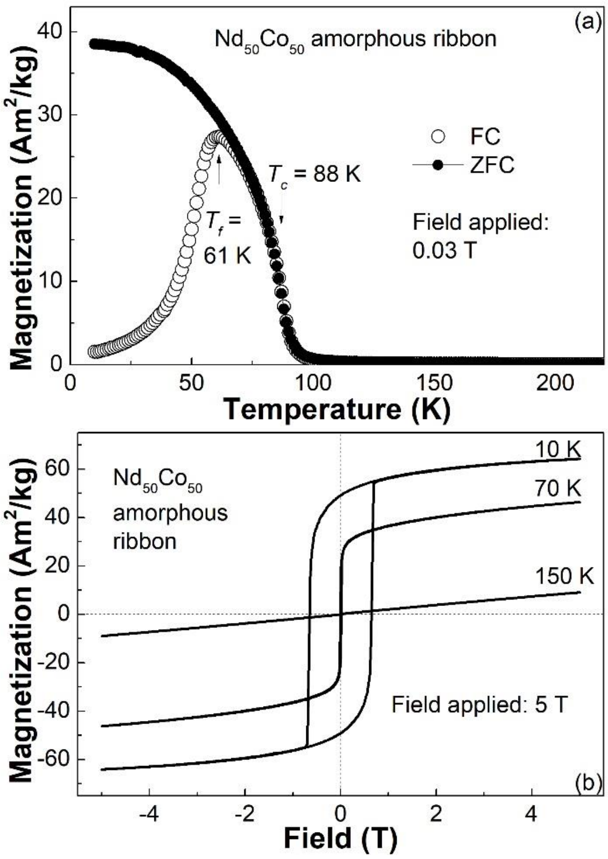
Figure 3 (a) The isothermal *M*-*H* curves of the $Nd_{50}Co_{50}$ amorphous ribbon measured at various temperatures under a magnetic field of 5 T; (b) The $(-\Delta S_m)$-T curves of the $Nd_{50}Co_{50}$ amorphous ribbon under different magnetic fields.

Figure 4 The magnetostriction plots with error bars of the $Nd_{50}Co_{50}$ amorphous ribbon measured at the temperature of 30 K, 40 K, 50 K and 60 K under a field of 5 T.



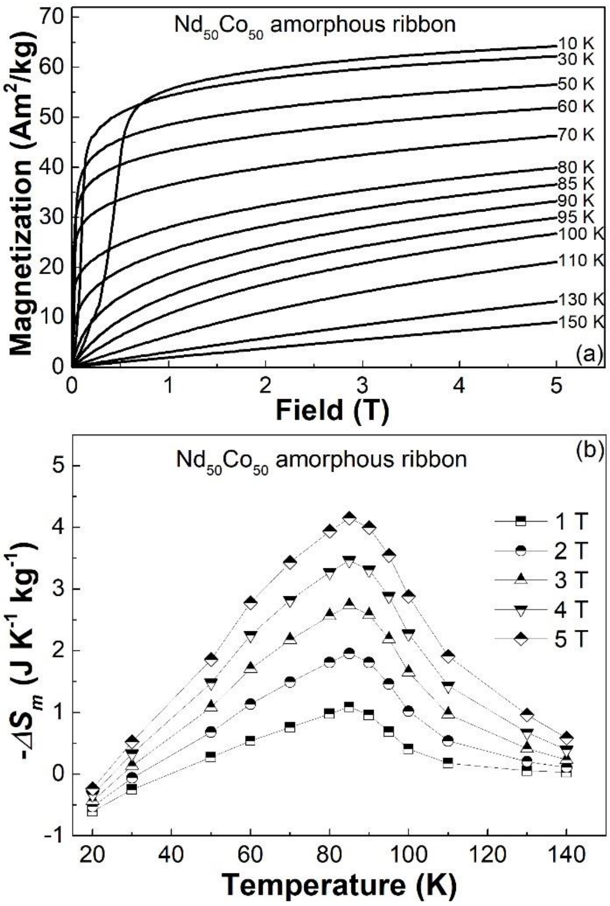
Q. Wang *et al*.

Figure 1



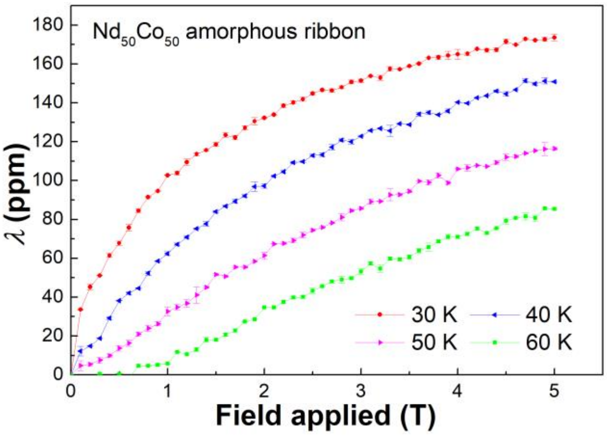
Q. Wang *et al*.

Figure 2



Q. Wang *et al*.

Figure 3



Q. Wang *et al*.

Figure 4

Figure 1

Click here to access/download;Figure;fig 1.jpg

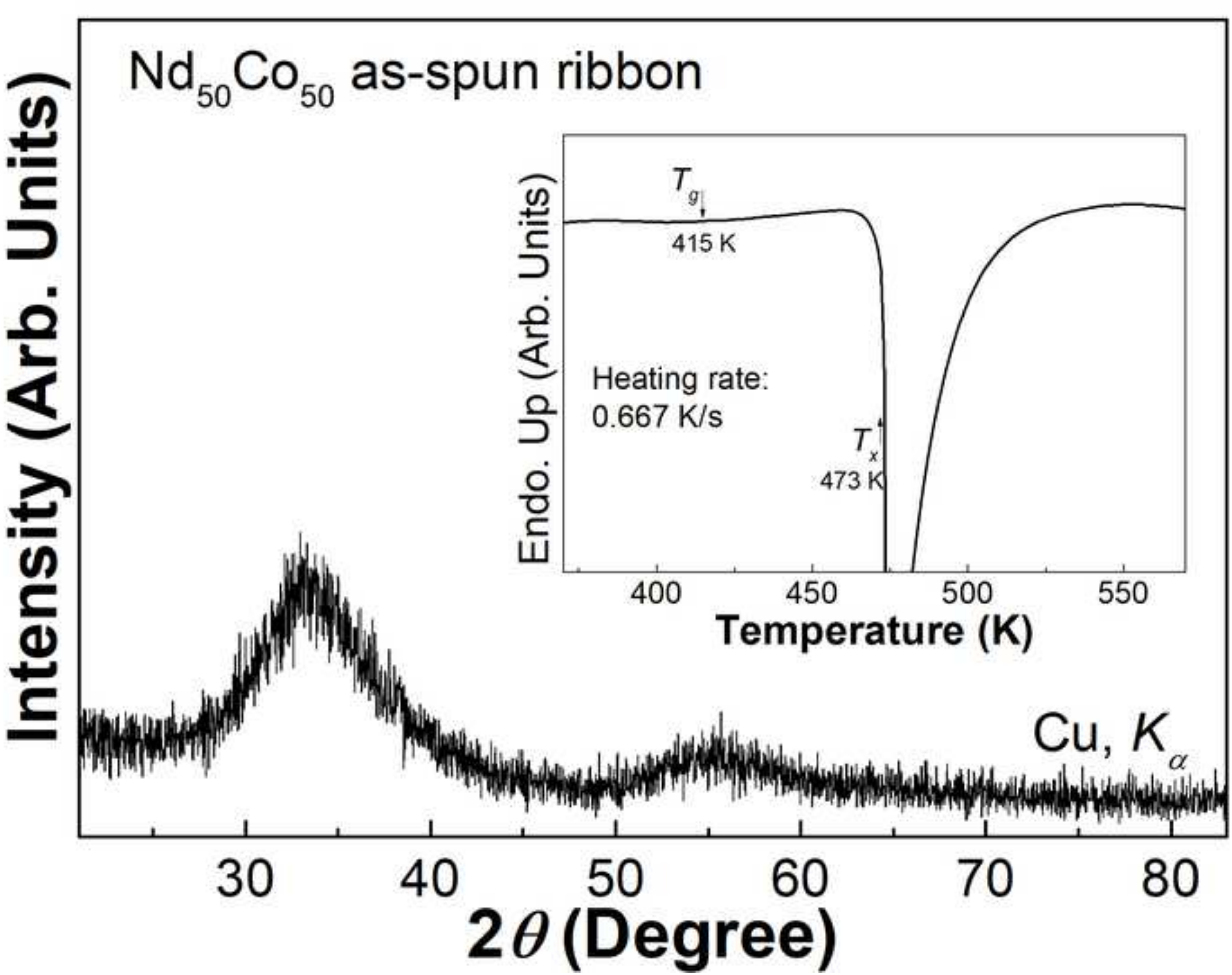


Figure 2a

[Click here to access/download;Figure;fig 2a.jpg]

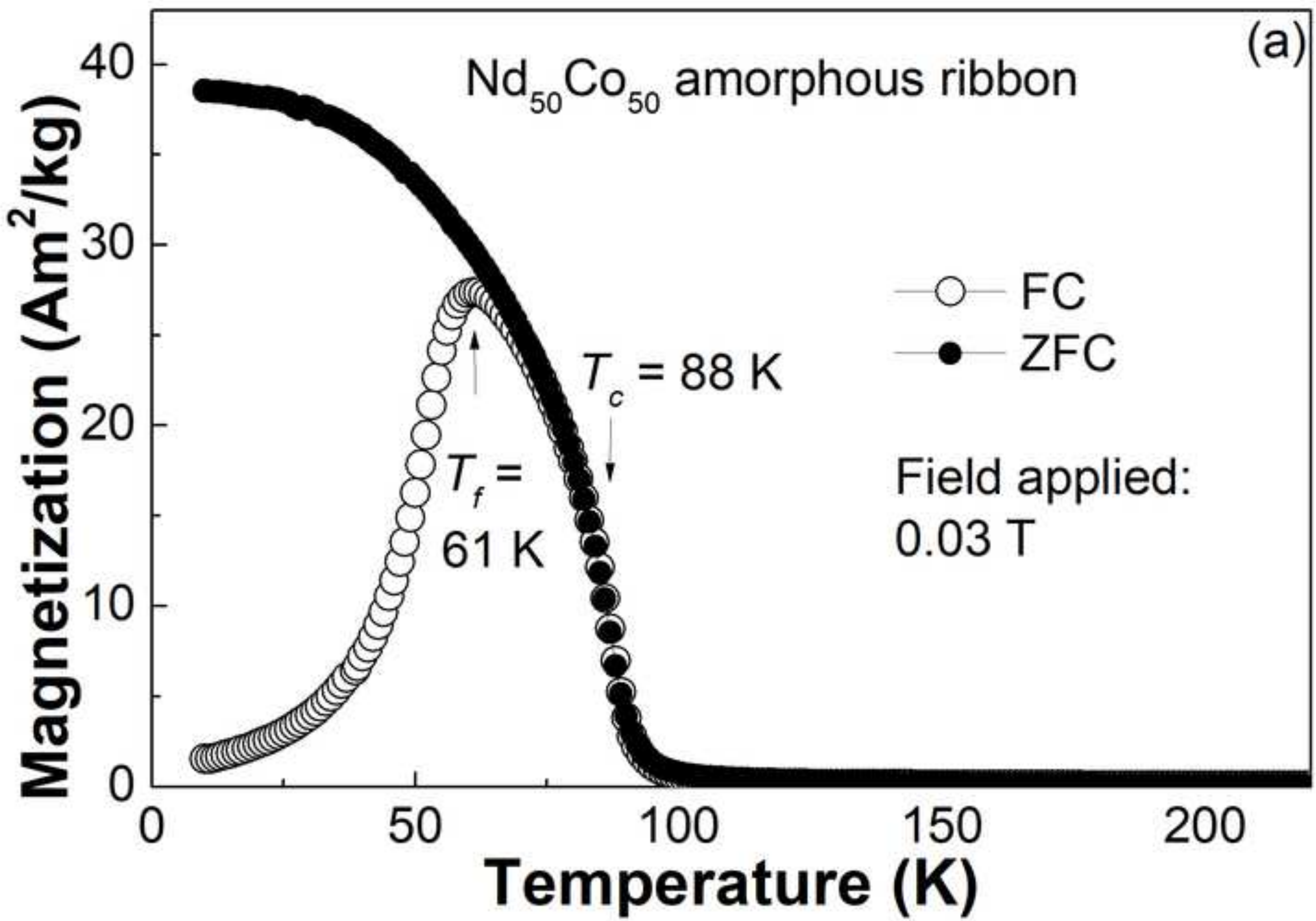


Figure 2b

Click here to access/download;Figure;fig 2b.jpg

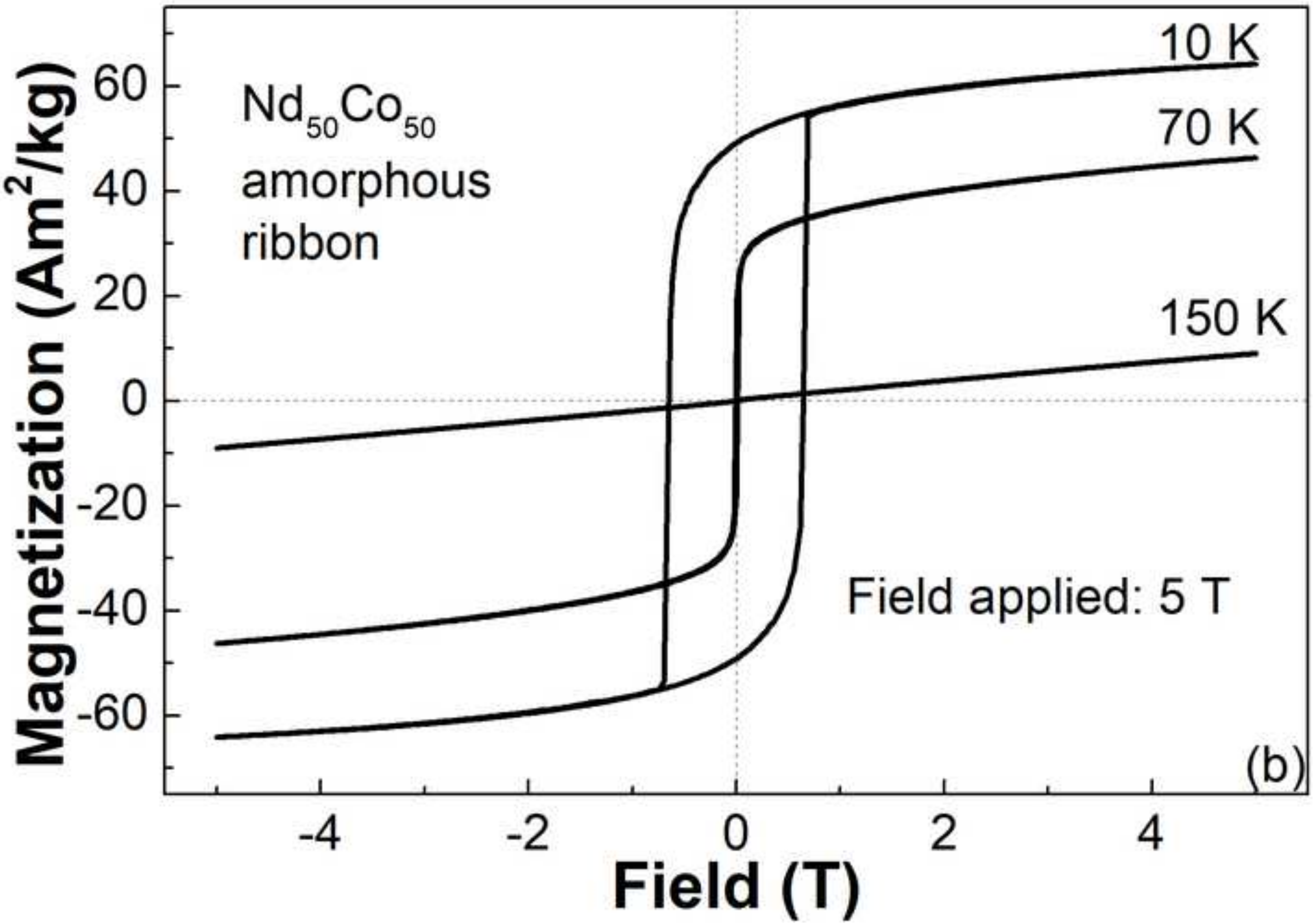


Figure 3a

Click here to access/download;Figure;fig 3a.jpg

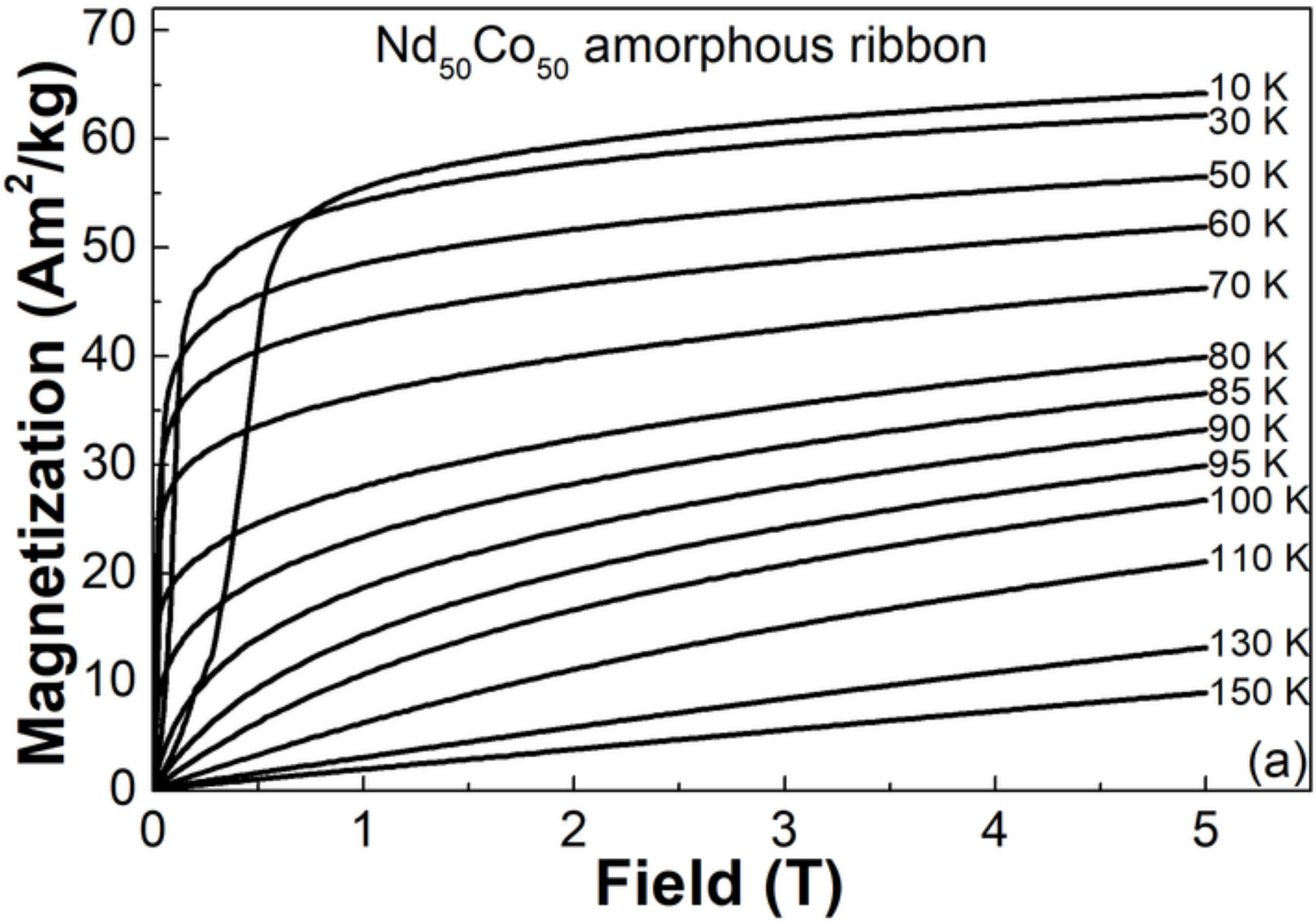


Figure 3b

Click here to access/download;Figure;fig 3b.jpg

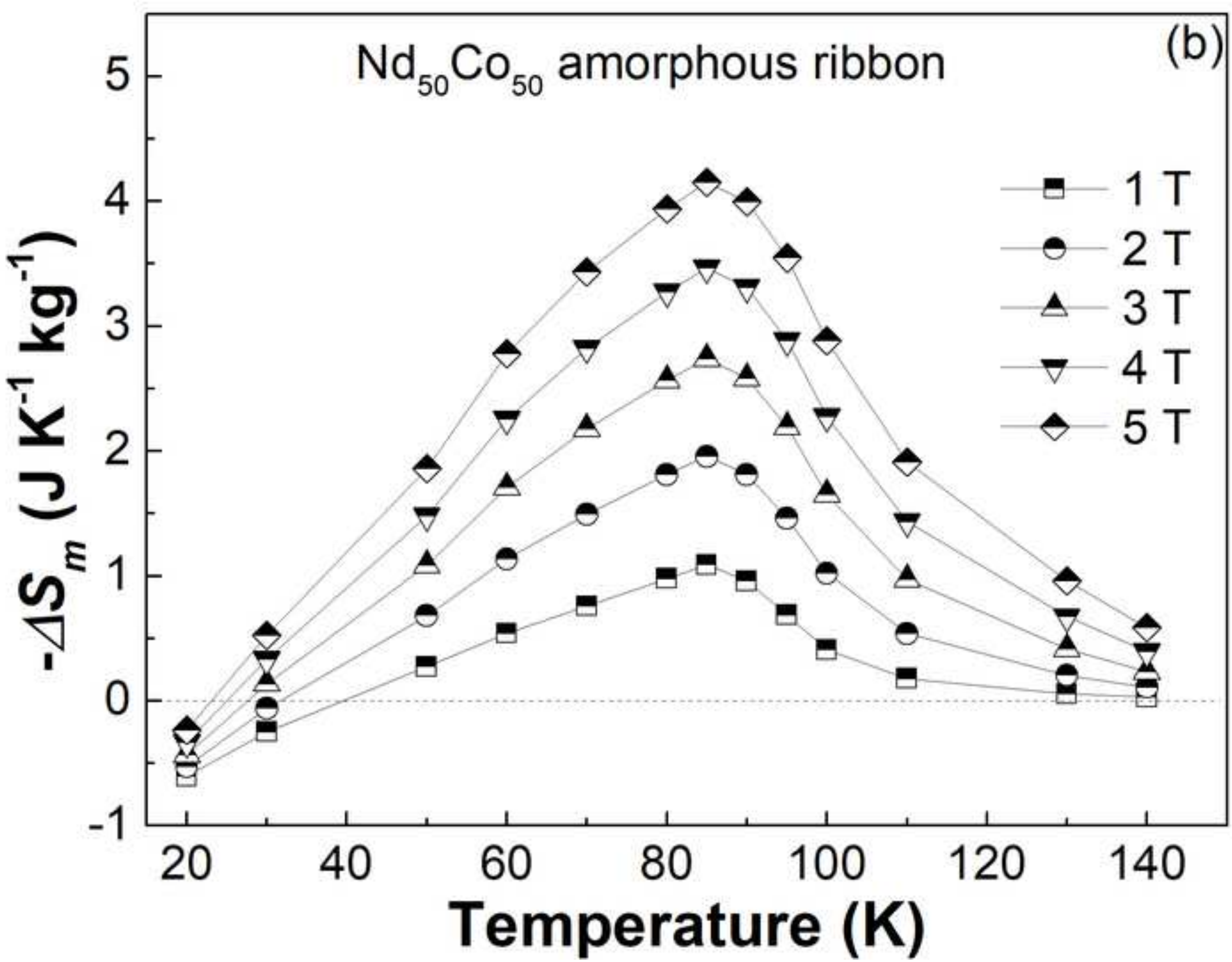


Figure 4-r1

Click here to access/download;Figure;fig 4-r1.jpg