



Cite this: *Chem. Commun.*, 2014, 50, 12734

Received 9th July 2014,
Accepted 29th August 2014

DOI: 10.1039/c4cc05281a

www.rsc.org/chemcomm

Epitaxial antiperovskite superconducting CuNNi₃ thin films synthesized by chemical solution deposition†

Zhenzhen Hui,^{‡a} Xianwu Tang,^{‡a} Dingfu Shao,^a Hechang Lei,^a Jie Yang,^a Wenhai Song,^a Hongmei Luo,^b Xuebin Zhu^{*a} and Yuping Sun^{*ac}

Epitaxial antiperovskite superconducting CuNNi₃ thin films have been grown by chemical solution deposition. The film is a type II superconductor and shows a T_c of 3.2 K with a transition of 0.13 K. The $H_{c2}(0)$ and ξ_0 are estimated to be 8.1 kOe and 201 Å, respectively.

Transition-metal nitrides and carbides have been known to exhibit lots of very important properties such as superconductivity, catalytic activity, unusual magnetic properties, and high hardness and mechanical strength.^{1–3} As typical transition-metal nitrides and carbides, antiperovskite structured materials have been studied intensively both by experimental and theoretical methods due to their rich physical properties as well as potential applications. Novel interesting properties, such as superconductivity in MgCNi₃ and SrPt₃,^{4,5} excellent magnetism in RhNFe₃,⁶ and giant negative thermal expansion in Cu_{1–x}Ge_xNMn₃,⁷ have been widely investigated. However, the intrinsic physical properties have not yet been well-studied because of the challenges in preparing antiperovskite single crystals as well as in preparing high-quality antiperovskite thin films.⁸ As for the antiperovskite superconducting materials, to date, to the best of our knowledge, only polycrystalline MgCNi₃ thin films have been successfully obtained by electron-beam evaporation⁹ and there has been no report on epitaxial growth of the antiperovskite superconducting thin films. In spite of a large amount of ferromagnetic Ni atoms in their unit cells, the nickel-based antiperovskite materials show superconductivity rather than magnetism. According to band-structure calculations, MgCNi₃ is near ferromagnetic instability due to the high density of states at the Fermi level.^{10,11} To investigate intrinsic superconducting

properties, it is desirable to develop an effective route to synthesize epitaxial antiperovskite superconducting thin films. Chemical solution deposition methods are effective methods with advantages of low-cost, easy set-up, and coating of large areas.^{12–15} However, it has never been tried to prepare antiperovskite thin films by chemical solution deposition methods. The development of an alternative synthesis route to prepare antiperovskite thin films is clearly technologically relevant to advance antiperovskite materials.

Here, we report the preparation of epitaxial superconducting antiperovskite CuNNi₃ (CNN) thin films on LaAlO₃ (LAO) substrates by chemical solution deposition. Thin films were annealed at 600 °C for 2 hours in air and nitrogenized at 600 °C for 2 hours under flowing ammonia with a pressure of 1 atm (see the ESI,† where the details of experimental procedures, characterization and theoretical calculations are presented). Recently, CNN ceramic was reported to be a superconductor with a superconducting temperature T_c of 3.2 K and a cubic antiperovskite structure with a lattice constant of 3.742 Å, as shown in the inset of Fig. 1a.¹⁶ The successful growth of phase pure antiperovskite CNN thin films by a controllable and reproducible synthesis route makes it possible to study their fundamental physical properties. This achievement is also a tremendous leap toward the utilization of chemical solution methods to prepare other novel antiperovskite thin films.

Epitaxial growth of CNN thin films on LAO was confirmed by X-ray diffraction (XRD). As shown in Fig. 1a, the presence of only the (002) peak from CNN indicates that the films are preferentially oriented along the *c*-axis. No detectable diffraction from undesirable phases such as Ni and Ni₄N suggests the formation of phase pure CNN. As shown in Fig. 1b in the ϕ -scans of CNN(110) and LAO(110) reflections, four peaks 90° apart confirm the formation of cubic CNN thin films, which are corresponding to the LAO peaks, suggesting the cube-on-cube growth mode. The epitaxial relationships between CNN and LAO were determined to be (001)CNN//[(001)LAO and [110]CNN//[110]LAO. The lattice parameter of CNN, calculated from the (002) peak, was $a = 3.75$ Å, which is the same as that of the bulk CNN ceramic.¹⁶ The lattice constant was also calculated by first-principles density functional theory (DFT) using the projected augmented-wave (PAW)

^a Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China. E-mail: xbzhu@issp.ac.cn, ypsun@issp.ac.cn

^b Department of Chemical Engineering, New Mexico State University, Las Cruces, New Mexico 88003, USA

^c High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, China

† Electronic supplementary information (ESI) available: Details of experimental procedures, characterization and theoretical calculations. See DOI: 10.1039/c4cc05281a

‡ These two authors contribute equally.

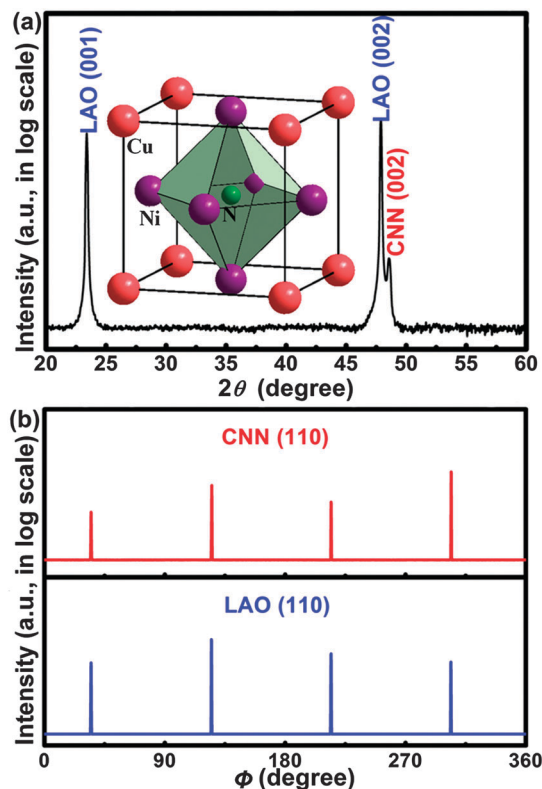


Fig. 1 (a) XRD θ - 2θ result of the CNN film on LAO(001) and the inset shows the crystal structure of CNN; (b) XRD ϕ -scans of (110) reflections of CNN and LAO.

method with a generalized gradient approximation (GGA) as implemented in the ABINIT code (see the ESI† for details). It was found that the lattice constant decreased upon decreasing the N content and the lattice of the stoichiometric CNN was calculated to be 3.76 Å, which is in very good agreement with the experimental result ($a = 3.75$ Å), indicating the stoichiometry of the derived epitaxial CNN thin films.

The microstructure and thickness of the derived CNN thin films were investigated by field-emission scanning electron microscopy (FE-SEM). As shown in Fig. 2a, it can be seen that the CNN film is relatively dense without obvious porosity. The thickness measured by a cross-sectional FE-SEM was determined to be 90 nm, as shown in the inset of Fig. 2a. To confirm the lattice constant calculated by XRD, it was also measured by transmission electron microscopy (TEM), as shown in Fig. 2b. The lattice constant was determined to be 3.75 Å both by the lattice stripes and the selected area electron diffraction (SAED), which is the same as that obtained from the XRD pattern. The stoichiometry of the CNN thin film was determined by electron dispersion spectroscopy (EDS). Due to the relatively large uncertainty for light elements in EDS,¹⁷ we just determined the atomic ratio of Cu:Ni, which was found to be 1:3.03 suggesting the stoichiometry for the derived CNN thin films.

Epitaxial CNN thin films exhibited different properties as compared to those of the bulk CNN ceramic. Fig. 3a shows the temperature dependence of resistivity for the derived CNN

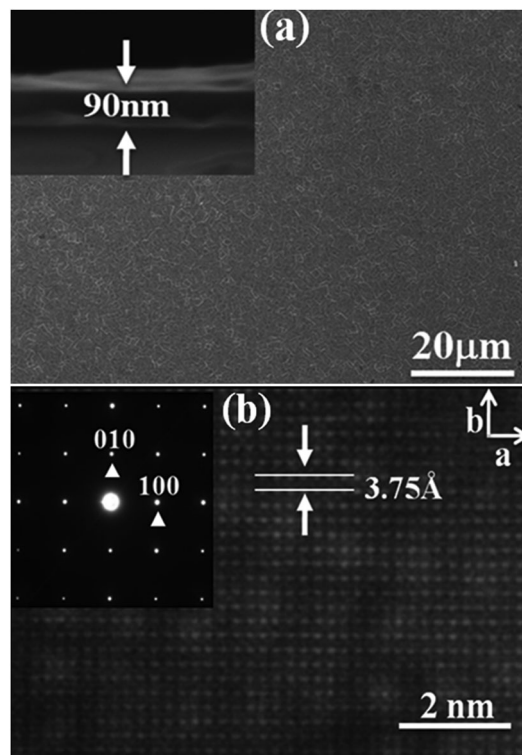


Fig. 2 (a) Surface FE-SEM result of CNN/LAO and the inset gives the thickness about 90 nm; (b) the surface HRTEM result of the CNN film and the inset shows the SAED pattern.

thin films. The CNN thin film shows a characteristic metal-like resistivity temperature above the superconducting transition. The resistivity at 300 K is 63.1 $\mu\Omega$ cm, which is about 5 times lower than that of the bulk CNN ceramic due to the decreased grain boundary scattering of carriers for epitaxial growth.¹⁶ The onset of superconductivity takes place at a T_c of 3.2 K (at which the resistivity deviates from the normal state resistivity) and the transition width ΔT is 0.13 K (between the 90% and 10% of the normal state resistivity), as shown in the inset of Fig. 3a, these results are similar to those of a previous report on the bulk CNN ceramic.¹⁶ Such a sharp transition indicates the high purity and high quality of the epitaxial CNN thin film. The normal state resistivity was fitted by different mechanisms. It was found that the resistivity at high temperature ($50 \text{ K} < T < 350 \text{ K}$) can be well fitted by the Bloch-Grüneisen expression¹⁸ $\rho^{-1} = \rho_p^{-1} + (\rho_0 + \rho_{ph})^{-1}$ in the case of Einstein phonon distribution, as shown in Fig. 3a, where $\rho_{ph} = \rho_1 \coth\left(\frac{\Theta_E}{2T}\right) \left[1 + \left(\frac{2}{3}\right) \sinh^2\left(\frac{\Theta_E}{2T}\right)\right]^{-1}$ and Θ_E , ρ_0 , ρ_p and ρ_1 are Einstein temperature, residual resistivity, parallel resistivity and a constant, respectively. The best fitting result gave $\Theta_E = 180.1$ K, $\rho_0 = 8.831$ $\mu\Omega$ cm, $\rho_p = 212.1$ $\mu\Omega$ cm and $\rho_1 = 25.1$ $\mu\Omega$ cm. The Einstein temperature Θ_E was comparable with that of MgCNi_3 ($\Theta_E = 206.1$ K).¹⁹ The low temperature resistivity ($5 \text{ K} < T < 50 \text{ K}$) gave a power law, $\rho = \rho_0^* + aT^n$ and the fitting result gave $\rho_0^* = 3.741$ $\mu\Omega$ cm and $n = 2.351$, which is also shown in Fig. 3a. The fitting results indicate that the electron-phonon scattering is the main contribution to the resistivity at high

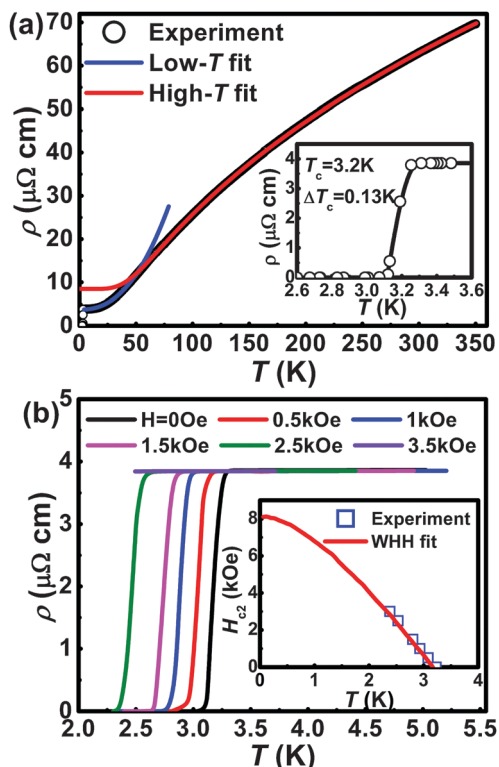


Fig. 3 (a) Temperature dependence of resistivity of the CNN film on LAO(001) under a zero field as well as the transport fitting results and the inset is the enlarged image to give a clear superconducting transition; (b) superconducting transition under different magnetic fields and the inset is the fitting result obtained by the WHH expression.

temperatures, and both the electron–phonon scattering and electron–electron scattering contribute simultaneously to the resistivity at low temperatures.^{20,21} According to the theoretically calculated results (see ESI[†]), similar to the case of MgCNi_3 ,^{10,11} there is a large density of states (DOS) at E_F ($N(E_F)$) in CNN. From the BCS theory, a large $N(E_F)$ can lead to a strong electron–phonon coupling.

The upper critical field (H_{c2} , the field at which a superconductor becomes normal) is a very important parameter for a superconductor. In order to determine the H_{c2} , the superconducting transition was measured as a function of magnetic field, as shown in Fig. 3b. The inset of Fig. 3b shows the H_{c2} corresponding to the temperatures where the resistivity drops to 50% of the normal state resistivity. According to the conventional one-band Werthamer–Helfand–Hohenberg (WHH) theory,²² which describes the orbital limited H_{c2} of a dirty type-II superconductor, H_{c2} is described by $H_{c2}(0) = -0.693 \left(\frac{dH_{c2}}{dT} \right)_{T_c} T_c$, where $H_{c2}(0)$ is the upper critical field at zero temperature. The fitting curve obtained by the WHH theory is also shown in the inset of Fig. 3b, giving an $H_{c2}(0)$ of 8.1 kOe. The superconducting coherence at zero temperature, ξ_0 , was estimated using the Ginzburg–Landau (GL) expression²³ $H_{c2}(0) = \Phi_0 / 2\pi\xi_0^2$ with $\Phi_0 = 2.07 \times 10^{-15}$ Wb, giving a ξ_0 of 201.1 Å. The decreased $H_{c2}(0)$ as compared to that of the bulk CNN ceramic ($H_{c2}(0) = 1.21$ T)¹⁶ suggests that there

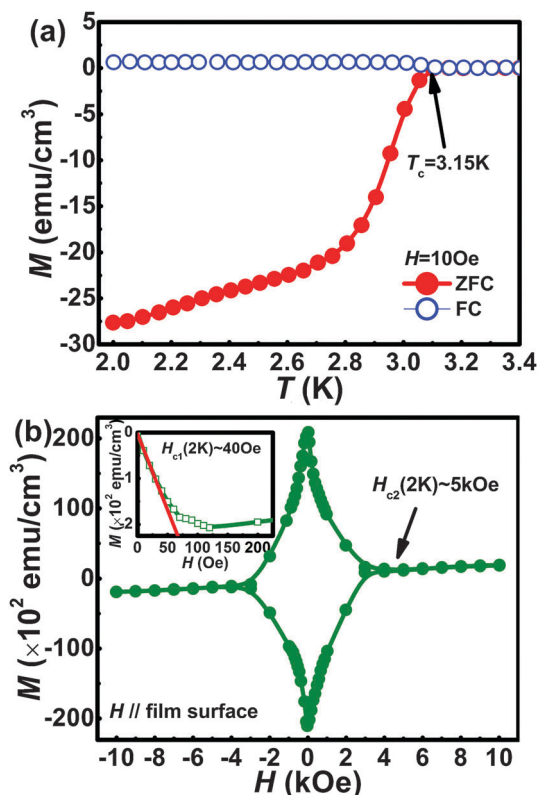


Fig. 4 (a) Temperature dependence of magnetism with FC and ZFC modes under 10 Oe applied magnetic field parallel to the surface; (b) the $M(H)$ loop at 2 K and the inset is the low-field $M(H)$ to give the H_{c1} at 2 K.

are less vortex pinning centres in epitaxial CNN thin films due to the reduced defects such as grain boundaries.

To further confirm the superconducting properties of the epitaxial CNN thin films, the temperature dependence of magnetization employing both FC (field-cooled) and ZFC (zero-field-cooled) protocols under an applied magnetic field of 10 Oe parallel to the film surface of the epitaxial CNN thin film was measured, and the results are shown in Fig. 4a. The film shows a superconducting onset temperature of 3.15 K in terms of FC and ZFC bifurcation, which is self-consistent with the T_c determined from the resistivity, further confirming the superconducting characteristic of the epitaxial CNN thin film. There is evidence for flux trapping too. The magnetic hysteresis loop $M(H)$ at 2 K, shown in Fig. 4b clearly indicates that the CNN film is a type II superconductor. The low critical field at 2 K $H_{c1}(2\text{ K})$ was determined to be ~ 40 Oe from the low field $M(H)$ at 2 K, as shown in the inset of Fig. 4b, by a linear fitting of the $M(H)$ curve at low field, which is the same as that reported in a previous study on CNN ceramics.¹⁶

In summary, high-quality epitaxial antiperovskite CuNNi_3 thin films have been synthesized by a chemical solution deposition method. The epitaxial CuNNi_3 thin films show a superconducting transition temperature of 3.2 K with a transition width of 0.13 K, a $H_{c2}(0)$ of 8.1 kOe, and a ξ_0 of 201 Å. The high temperature resistivity is mainly dominated by the electron–phonon scattering and the resistivity at low temperatures is controlled by both the

electron–phonon and the electron–electron scattering. The reported chemical solution deposition of epitaxial antiperovskite CuNNi₃ thin films will enable extensive fundamental investigation of the properties and will provide a very simple and low-cost method to prepare other epitaxial antiperovskite thin films.

This work was supported by the National Basic Research Program of China (2014CB931704 and 2011CBA00111) and by the National Nature Science Foundation of China under Contract No. 51171177 and 11174288. H. Luo acknowledges the funding support from NSF under Grant No. 1131290.

Notes and references

- 1 R. Niewa and H. Jacobs, *Chem. Rev.*, 1996, **96**, 2053.
- 2 M. Shalom, V. Molinari, D. Esposito, G. Clavel, D. Ressnig, C. Giordano and M. Antonietti, *Adv. Mater.*, 2014, **26**, 1272.
- 3 D. Choi, G. E. Blomgren and P. N. Kumta, *Adv. Mater.*, 2006, **18**, 1178.
- 4 T. He, Q. Huang, A. P. Ramirez, Y. Wang, K. A. Regan, N. Rogado, M. A. Hayward, M. K. Haas, J. S. Slusky, K. Inumara, H. W. Zandbergen, N. P. Ong and R. J. Cava, *Nature*, 2001, **411**, 54.
- 5 T. Takayama, K. Kuwano, D. Hirai, Y. Kutsura, A. Yamamoto and H. Takagi, *Phys. Rev. Lett.*, 2012, **108**, 237001.
- 6 A. Houben, P. Muller, J. V. Appen, H. Lueken, R. Niewa and R. Dronskowski, *Angew. Chem., Int. Ed.*, 2005, **44**, 7212.
- 7 S. Likubo, K. Kodama, K. Takenaka, H. Takagi, M. Takigawa and S. Shamoto, *Phys. Rev. Lett.*, 2008, **101**, 205901.
- 8 H. S. Lee, D. J. Jang, H. J. Lee, S. I. Lee, S. M. Choi and C. J. Kim, *Adv. Mater.*, 2006, **19**, 1807.
- 9 D. P. Young, M. Moldovan, D. D. Craig and P. W. Adams, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2003, **68**, 020501.
- 10 H. Rosner, R. Weht, M. D. Johannes, W. E. Pickett and E. Tosatti, *Phys. Rev. Lett.*, 2001, **88**, 027001.
- 11 D. J. Singh and I. I. Mazin, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **64**, 140507.
- 12 H. M. Luo, H. Y. Wang, Z. X. Bi, D. M. Feldman, Y. Q. Wang, A. K. Burrell, T. M. McCleskey, E. Bauer, M. E. Hawley and Q. X. Jia, *J. Am. Chem. Soc.*, 2008, **130**, 15224.
- 13 G. Zou, M. Jain, H. Zhou, H. Luo, S. Baily, L. Civale, E. Bauer, T. McCleskey, A. Burrell and Q. X. Jia, *Chem. Commun.*, 2008, 6022.
- 14 Y. Y. Zhang, N. Haberkorn, F. Ronning, H. Y. Wang, N. A. Mara, M. J. Zhuo, L. Chen, J. H. Lee, K. J. Blackmore, E. Bauer, A. K. Burrell, T. M. McCleskey, M. E. Hawley, R. K. Schulze, L. Civale, T. Tajima and Q. X. Jia, *J. Am. Chem. Soc.*, 2011, **133**, 20735.
- 15 H. M. Luo, Y. Lin, H. Y. Wang, J. H. Lee, N. A. Suvorova, A. H. Mueller, A. K. Burrell, T. M. McCleskey, E. Bauer, I. O. Usov, M. E. Hawley, T. G. Holesinger and Q. X. Jia, *Adv. Mater.*, 2009, **21**, 193.
- 16 B. He, C. Dong, L. H. Yang, X. C. Chen, L. H. Ge, L. B. Mu and Y. G. Shi, *Supercond. Sci. Technol.*, 2013, **26**, 125015.
- 17 R. Al-Merey, J. Karajou and H. Issa, *Appl. Radiat. Isot.*, 2005, **62**, 501.
- 18 M. Affronte, J. Marcus and C. Escribano-Filippini, *Solid State Commun.*, 1993, **85**, 501.
- 19 S. Y. Li, R. Fan, X. H. Chen, C. H. Wang, W. Q. Mo, K. Q. Ruan, Y. M. Xiong, X. G. Luo, H. T. Zhang, L. Li, Z. Sun and L. Z. Cao, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **64**, 132505.
- 20 H. M. Luo, H. Y. Wang, Z. Bi, G. F. Zou, T. M. McCleskey, A. K. Burrell, E. Bauer, M. E. Hawley, Y. Wang and Q. X. Jia, *Angew. Chem., Int. Ed.*, 2009, **48**, 1490.
- 21 P. A. Lee and T. V. Ramakrishnan, *Rev. Mod. Phys.*, 1985, **57**, 287.
- 22 N. R. Werthamer, E. Helfand and P. C. Hohenberg, *Phys. Rev.*, 1966, **147**, 295.
- 23 D. P. Hampshire, in *Handbook of Superconducting Materials*, ed. D. Cardwell, IOP, Bristol, 2002.