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Citation: [Applied Physics Letters](#) **104**, 053105 (2014); doi: 10.1063/1.4863966

View online: <http://dx.doi.org/10.1063/1.4863966>

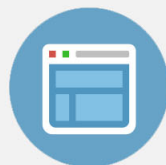
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Paramagnetic Cu-doped Bi₂Te₃ nanoplates

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(Received 14 December 2013; accepted 20 January 2014; published online 3 February 2014)

Uniform Cu-doped Bi₂Te₃ hexagonal nanoplates with widths of ~ 200 nm and thicknesses of ~ 20 nm were synthesized using a solvothermal method. According to the structural characterization and compositional analysis, the Cu²⁺ ions were found to substitute Bi³⁺ ions in the lattice. High-level Cu doping induces a lattice distortion and decreases the crystal lattice by 1.17% in the *a* axis and 2.38% in the *c* axis. A paramagnetic state is observed in these nanoplates from 2 to 295 K, which is a significant difference from their diamagnetic un-doped Bi₂Te₃. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4863966>]

As an ideal candidate for applications in thermoelectrics or topological insulators, Bi₂Te₃ has been a hottest material system in modern physics and material science.¹ Especially, Bi₂Te₃ has been demonstrated to have a conducting surface state with a single non-degenerate Dirac cone with linear dispersion in the momentum space.¹ The unique physical phenomena, such as quantized anomalous Hall effect^{2–4} and topological magnetoelectric effect,^{5–7} have been theoretically predicted and subsequently demonstrated by experiments in the engineered Bi₂Te₃. Among them, introduction of magnetic impurities into these materials can induce the breaking of the time reversal symmetry and result in a gap at the Dirac point of the topological surface state, which finally realize more exotic phenomena mentioned above.^{2–12} Therefore, the coexistence of both magnetic moment and topological state in these materials, even at the nanoscale, is exciting for the design and development of future spintronic devices.

Extensive studies have shown that transition metal doping in Bi₂Te₃ can tune their electron and phonon transport properties.^{13–17} Especially, transition metals, such as Fe,^{8,18–20} Cr,^{21–23} Mn,^{13,24–26} V,²⁷ Sn,²⁸ and Cu,¹⁴ have been widely substituted into bulk Bi₂Te₃ to produce magnetic-manipulated topological semiconductors, and most of them were realized by doping the transition metals into the bulk or thin film Bi₂Te₃ materials by conventional methods, such as the Bridgman growth,²⁹ vertical gradient solidification,²⁵ and vapor-liquid-solid methods.²⁰ So far, only very few magnetic doped Bi₂Te₃ nanomaterials have been reported.³⁰ In fact, as for the bulk topological insulator materials, the direct manipulation of their edge/surface states is relatively difficult due to significant outnumbering of the bulk carriers.^{31–35} Therefore, nano-engineered Bi₂Te₃ topological insulators not only reveal more enhanced and unique physical properties,^{36–38} but also lead to potential breakthroughs in the future spintronic applications. Very recently, enhanced surface conduction by manipulating the surface states in Bi₂Te₃ nanoribbons³¹ and Bi₂Te₃ nanoplates³⁹ synthesized by a solvothermal method were demonstrated.

Ferromagnetic ordering at the high Curie temperature (up to 45 K) was also reported in Mn²⁺/Mn³⁺ substituted Bi₂Te₃ nanoplates.³⁰ Therefore, it is anticipated that the doping of non-magnetic impurities into Bi₂Te₃ nanomaterials, such as Cu, may also advance the applications of Bi₂Te₃ nanomaterials in spintronics and result in new physical phenomena.

In this study, we demonstrate that Cu²⁺ can be readily doped into Bi₂Te₃ hexagonal nanoplates by a low-cost and controllable solvothermal method. Through detailed structural and compositional characterizations, the Cu²⁺ ions are found to substitute for the Bi³⁺ ions, which not only lead to a decrease of the lattice parameters in the Bi₂Te₃ crystal structure, but also cause atomic moment in the Bi₂Te₃ lattice which lead the paramagnetic behavior of the Cu-doped Bi₂Te₃ nanoplates from 2 to 295 K.

The Cu-doped Bi₂Te₃ nanoplates were synthesized using precursors of analytical grade Bi₂O₃, Te, CuCl₂, ethylene glycol, polyvinylpyrrolidone (PVP), NaBH₄, and NaOH solution. ~ 0.2 g of PVP was first dissolved in ethylene glycol (36 ml) to form a clear solution, followed by the additions of Bi₂O₃, CuCl₂, and Te powders in defined ratios. After stirring for 5 min, the prepared solution was mixed with 4 ml of NaOH solution (~ 5 mol/l), the resulting suspension was stirred vigorously for 30 min at 65 °C, and subsequently mixed with 0.05 g of NaBH₄ powders and sealed in a 120 ml steel autoclave. The autoclave was then heated to 230 °C and maintained at this temperature for various durations (up to 24 h), then cooled naturally to the room temperature. The synthesized products were collected by a high-speed centrifugation, washed 6 times with distilled water and absolute ethanol, and finally dried at 50 °C for 48 h in an oven. As a comparison, a similar synthesis procedure without CuCl₂ addition was used to fabricate un-doped Bi₂Te₃ nanoplates. The structural and chemical characteristics of synthesized products were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM, JEOL 7800F, acceleration voltage of 5 kV); transmission electron microscopy [TEM, Philips FEI Tecnai F20 (acceleration voltage of 200 kV) equipped with an electron energy loss spectroscopy (EELS) system for compositional analysis]; and X-ray photoelectron spectroscopy (XPS).

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Figure 1(a) is typical XRD patterns of synthesized doped and un-doped samples, in which all XRD peaks can be indexed exclusively as the rhombohedral structured Bi_2Te_3 phase, indicating the high purity of the synthesized products. The careful analysis of the two XRD patterns gives the lattice parameters of the Cu-doped Bi_2Te_3 nanostructures being $a = 4.33 \text{ \AA}$ and $c = 29.75 \text{ \AA}$, which are decreased by 1.17% in the a axis and 2.38% in the c axis when compared with the un-doped Bi_2Te_3 ($a = 4.386 \text{ \AA}$ and $c = 30.478 \text{ \AA}$). Figure 1(b) is a typical SEM image of synthesized Cu-doped Bi_2Te_3 nanostructures and shows a high density of nanoplates. Figure 1(c) is a high magnification SEM image, in which hexagonal shaped nanoplates with lateral dimension of $\sim 200 \text{ nm}$ and a thickness of $\sim 20 \text{ nm}$ can be clearly observed. To understand structural characteristics of such hexagonal nanoplates, detailed TEM characterizations were carried out. Figure 1(d) is a bright-field (BF) TEM image of a typical hexagonal nanoplate. Figure 1(e) is the corresponding selected area electron diffraction (SAED) pattern and indicates that the surface normal of the hexagonal nanoplate is parallel to its c axis and the six side edges can be determined to be $\{10\bar{1}0\}$ facets by correlating the TEM image and the SAED pattern. It should be noted that weak diffraction spots can be seen in Fig. 1(e). These weak spots may be caused (1) by the projection of diffractions from higher Lane zone(s) due to the large lattice parameter along the c axis and very thin TEM foil (20 nm) of the Bi_2Te_3 nanoplates along the c axis, or (2) by the antisite

defects or incomplete layers.⁴⁰ For this reason, these weak diffraction spots, which should be forbidden diffractions in the zero Lane zone, are not indexed. Figure 1(f) is the corresponding high resolution TEM image and confirms that the product is highly crystalline.

To clarify chemical characteristics of synthesized Cu-doped Bi_2Te_3 nanoplates, EELS was employed to determine the elemental specification and distribution within the hexagonal nanoplates. Figure 2(a) shows a BF TEM image of a typical Cu-doped Bi_2Te_3 hexagonal nanoplate. Figure 2(b) shows its corresponding EELS spectrum. In comparison, EELS spectra taken, respectively, from a Cu nanoparticle and a CuTe nanoplate are also shown in Fig. 2(b). It should be noted that EELS is a powerful technique for identifying the oxidation states of a transition metal from its near-edge fine structure, such as the L_3/L_2 edges.^{41–43} Through carefully analyzing the obtained EELS profiles (particular from a Cu particle and from a CuTe nanoplate), the Cu fine structure in non-zero oxidation states, such as Cu^{2+} , shows distinct, intense, and sharp L_3/L_2 edges.^{41,42} As can be seen from Fig. 2(b), the Cu L_3 peak of a Cu-doped Bi_2Te_3 nanoplate, located at $\sim 931 \text{ eV}$, is coincided with the Cu L_3 peak of the CuTe nanoplate, indicating that Cu^{2+} has been doped into Bi_2Te_3 lattice during the synthesis. It should be noted that the weak Cu L_2 peak (located at $\sim 952 \text{ eV}$) of the CuTe is not seen in the EELS profile of the Cu-doped Bi_2Te_3 nanoplate. This should be due to the low level of Cu doping in our

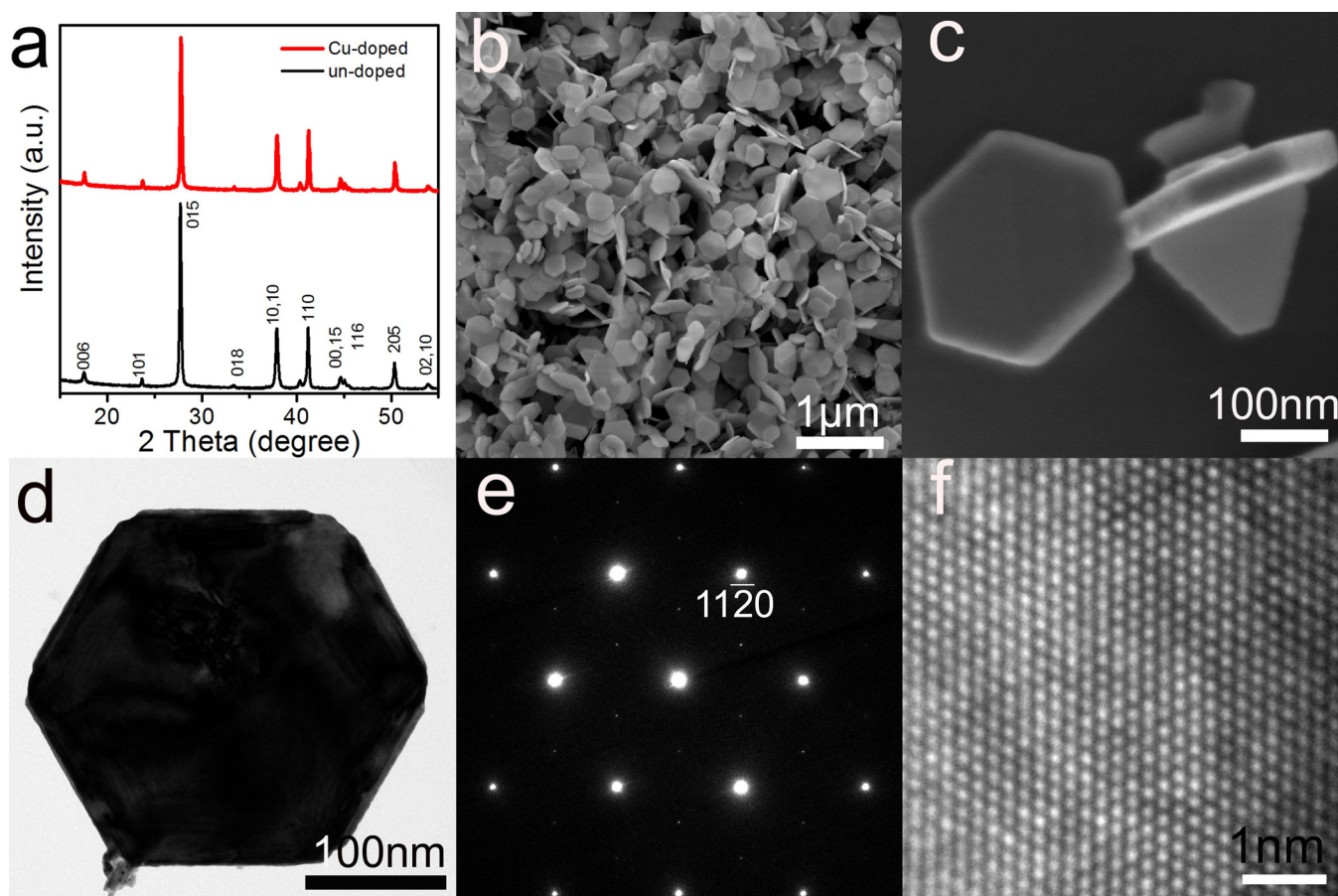


FIG. 1. Structural characteristic of Cu-doped Bi_2Te_3 samples: (a) Typical XRD patterns of the as-prepared doped and un-doped Bi_2Te_3 samples; (b) Low-magnification top-view SEM image; (c) High-magnification side-view SEM image; (d) Low-magnification TEM image for a typical Cu-doped Bi_2Te_3 nanoplate; (e) SAED pattern; (f) High-resolution TEM image for the nanoplate.

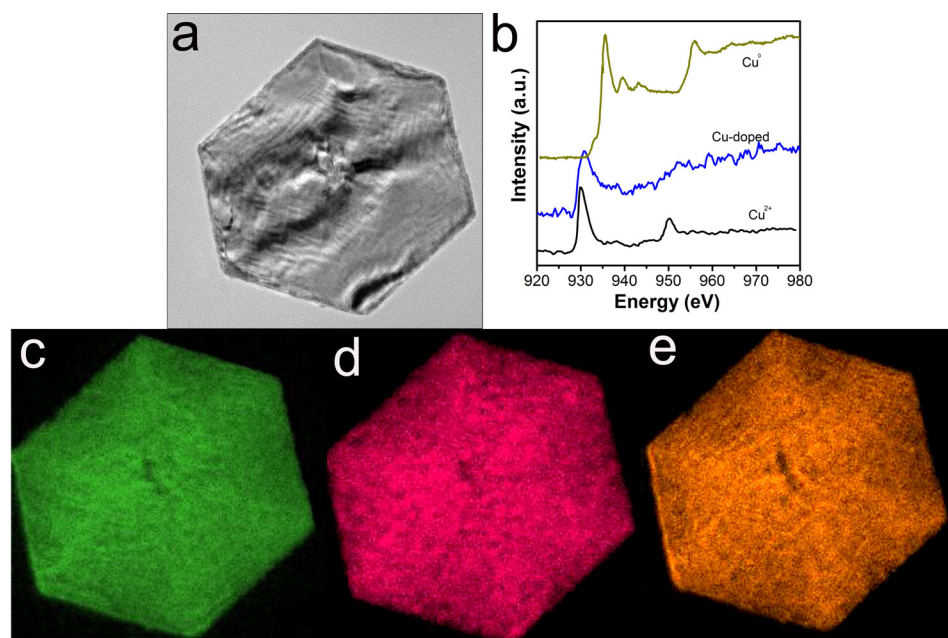


FIG. 2. Component analyses of the as-prepared Cu-doped Bi_2Te_3 nanoplates. (a) Bright-field TEM image for a typical as-prepared Cu-doped nanoplate with a thickness of less than 20 nm; (b) EELS spectra of Cu with reference EELS spectra for Cu metal (up) and Cu^{2+} (bottom) from CuTe nanoplates; (c)–(e) EELS mapping of Bi, Te and Cu.

Bi_2Te_3 nanoplates when compared with a significant amount of Cu^{2+} in the CuTe nanoplate. To further clarify the distribution of the elements Bi, Te, and Cu in this nanoplate, EELS maps were collected and are shown in Figs. 2(c)–2(e), respectively. From the contrast of Fig. 2(e), Cu is uniformly distributed within the nanoplate.

To understand the doping state of Cu and their bonding behavior in the Cu-doped Bi_2Te_3 nanoplates, XPS was performed and an example is shown in Fig. 3(a), in which the predominant measured binding energies for Bi and Te are 157.8 eV for Bi 4f and 573.7 eV for Te 3d, respectively; which correspond to the Bi_2Te_3 phase.^{44,45} In the XPS profile, a small peak associated with Cu 2p is seen. Figure 3(b) is the high-resolution XPS scan around the Cu 2p spectra, which shows two obvious satellite peaks, which can be indexed as the Cu^{2+} state, not Cu^0 state.⁴¹ Through the quantitative analysis of the XPS spectra, the composition of the Cu-doped Bi_2Te_3 nanoplate can be estimated as $\sim 38.4\%$, $\sim 59.9\%$, and $\sim 1.6\%$ for Bi, Te, and Cu, respectively; which is equivalent to an atomic ratio of Bi:Te:Cu of 1.92:3:0.08. Therefore, the composition of the sample can be defined as $\text{Bi}_{1.92}\text{Cu}_{0.08}\text{Te}_3$, in which the Cu ions substituted the Bi ions in the Bi_2Te_3 lattice. In fact, the ionic radii of Cu^{2+} are smaller than that of Bi^{3+} , so that Cu ions substituting for Bi

ions lead to decreased lattice parameters of the synthesized products, which is consistent with the obtained XRD patterns.

Based on the detailed structural, chemical, and bonding characterizations outlined above, we have achieved Cu-doped Bi_2Te_3 nanoplates with Cu^{2+} replacing Bi^{3+} . A few Cu doped bismuth chalcogenides have been reported and they have shown unique properties, such as superconductivity at 3.5 K^{46–49} and weak ferromagnetic state.¹⁴ Therefore, as for our Cu-doped Bi_2Te_3 nanoplates, magnetic properties may be expected. A Superconducting Quantum Interference Device (SQUID) magnetometer was used to examine temperature dependent magnetization in zero-field cooled (ZFC) and field cooled (FC) processes, Figure 4(a) is the ZFC and FC plots as a function of temperature, obtained by cooling the sample in the absence of a magnetic field from 295 K and then the magnetization was measured from 2 to 16 K under a magnetic field of 100 Oe. Figure 4(b) shows the magnetic field dependence of the magnetization and hysteresis loops at 2 K and room temperature (295 K), respectively. Based on both Figs. 4(a) and 4(b), the Cu-doped Bi_2Te_3 nanoplates show several characteristic features. (i) From the ZFC and FC curves, no any turning point can be observed within the temperature range of 2–16 K, indicating that the Cu-doped Bi_2Te_3 nanoplates have a similar magnetic state in this

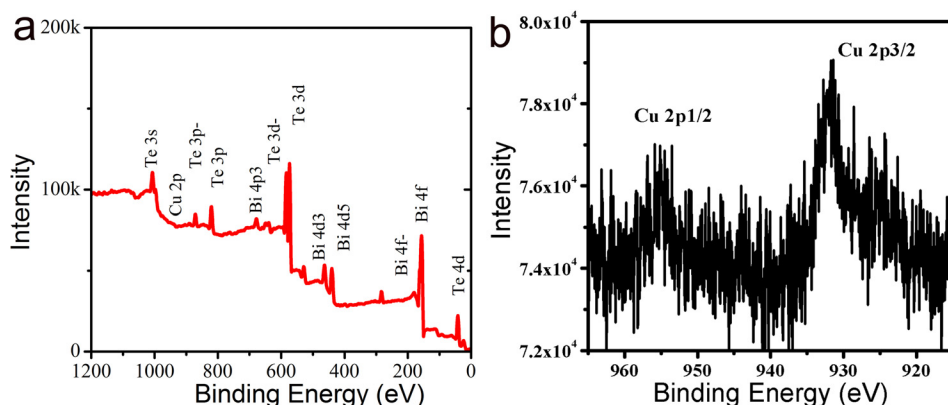


FIG. 3. XPS on an ensemble of Cu-doped Bi_2Te_3 nanoplates (a) confirms lower concentrations (1.6%) and (b) shows satellite peaks, which are evidence of Cu^{2+} , confirming the absence of Cu^0 .

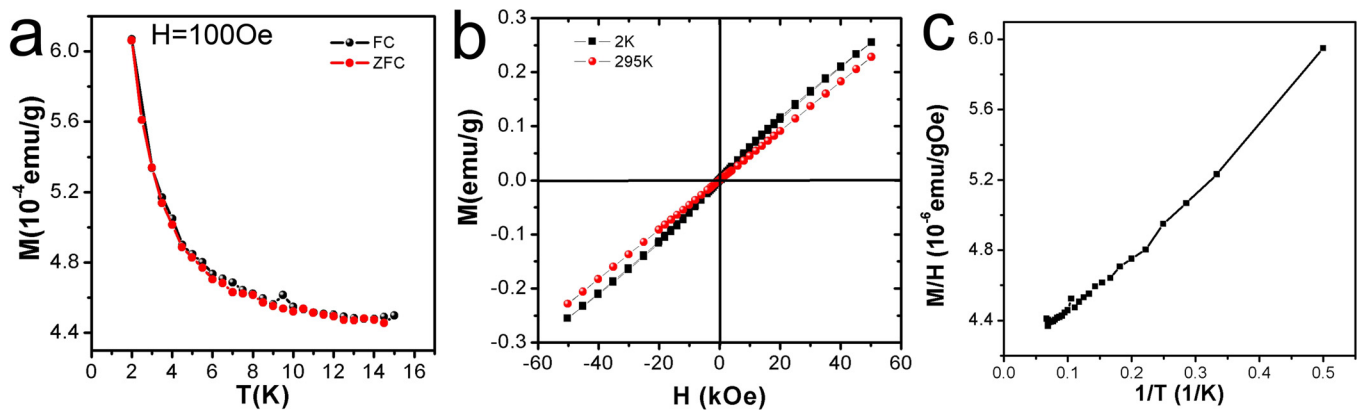


FIG. 4. Magnetic properties of the Cu-doped Bi_2Te_3 as-prepared nanoplates: (a) The temperature dependent magnetization moments in ZFC and FC processes under the field of 100 Oe; (b) The M-H profile at 2 K and room temperature; and (c) H/M plot of ZFC curve under the field of 100 Oe as a function of $(1/T)$, so that the slope corresponds to the Curie constant.

temperature range. (ii) The M-H curve demonstrates the typical paramagnetic behavior of Cu-doped Bi_2Te_3 nanoplates at $T = 2$ K and 295 K, from which the magnetization can be estimated over 0.25 emu/g under 50 kOe, which is higher than those currently reported values.¹⁴ (iii) A paramagnetic behavior of Cu-doped Bi_2Te_3 nanoplates was observed at room temperature, which is different from the Cu doped bulk Bi_2Te_3 .¹⁴ (iv) The fact of the magnetic similarity observed from 2 to 16 K and from the room temperature indicates that our Cu-doped Bi_2Te_3 nanoplates show the paramagnetic characteristic from 2 K to room temperature. As mentioned above, Cu^{2+} ions are doped in the nanoplates, so that the moments were considered to originate from doped Cu ions, and Curie constant (C) can be determined. According to the Curie law, the Curie constant can be expressed as⁵⁰

$$C = MT/H, \quad (1)$$

where M is the resultant magnetization, H is the magnetic field, and T is absolute temperature (K). To determine C , Fig. 4(a) is re-plotted into Fig. 4(c), so that C is the slope of the plot shown in Fig. 4(c), which can be determined as $C = 3.46 \times 10^{-6} \text{ emu K/g Oe}$. Furthermore, with the Langevin paramagnetic function, the susceptibility of the paramagnetic materials in a small field can be expressed as⁵⁰

$$\chi = N\mu_0\mu^2/(3k_B T) = M/H, \quad (2)$$

where χ is susceptibility, N is the number of magnetic atoms per unit gram (note: in our Cu-doped Bi_2Te_3 , the Cu doping level has been estimated by its determined composition— $\text{Bi}_{1.92}\text{Cu}_{0.08}\text{Te}_3$, so that the number of Cu ions in our $\text{Bi}_{1.92}\text{Cu}_{0.08}\text{Te}_3$ can be estimated as 6.079×10^{19} per unit gram), μ is the effective moment of a magnetic atom, μ_0 is vacuum permeability which is 1 in the centimetre–gram–second unit system and is dimensionless, and k_B is Boltzmann constant ($1.38 \times 10^{-23} \text{ J/K}$). According to Eq. (1), $M/H = C/T$, which can be used in Eq. (2), from which $\mu = 4.452 \times 10^{-24} \text{ J/T}$ can be calculated. Because the pure Bi_2Te_3 is a diamagnetism material, the observed magnetic moment was considered to come from the doped Cu ion in the Bi_2Te_3 , we can definite that the every doped Cu ion in our $\text{Bi}_{1.92}\text{Cu}_{0.08}\text{Te}_3$ system has an effective moment of $\mu = x\mu_B$, where x is the amount of

Bohr magneton from each doped Cu ion and μ_B is the Bohr magneton ($9.274 \times 10^{-24} \text{ J/T}$).⁵⁰ Therefore, x can be determined as 0.48, meaning that every Cu ion has an effective moment of $0.48\mu_B$ in our Cu-doped Bi_2Te_3 . Therefore, the magnetic moments originated from the doped Cu^{2+} ions and the paramagnetic behavior are contributed from the spin polarization of electric band structure. These findings of paramagnetic Cu-doped Bi_2Te_3 nanoplates should be a significant progress in the field of electronics and spintronics.

In summary, the uniform Cu-doped Bi_2Te_3 hexagonal nanoplates were synthesized by a green and simple solvothermal method. Based on the structural, chemical, and bonding characteristics, the fact that smaller Cu^{2+} ions were substituted the Bi^{3+} ions in the crystal lattice leads to reduced lattice parameters. The Cu doping in the Bi_2Te_3 nanoplates causes paramagnetic state from 2 K to the room temperature. This study paves a way to develop magnetic Bi_2Te_3 topological insulators for design and development of future electronic and spintronic devices.

This work was supported by the Australian Research Council. Z.G.C. would thank the QLD government for a smart state future fellowship and a UQ research foundation excellent award. This work was also supported by the National Natural Science Foundation of China (No. 51271178) and the National Basic Research Program (No. 2010CB934603) of China. The authors acknowledge the Australian Microscopy & Microanalysis Research Facility for providing characterization facilities.

¹H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, *Nat. Phys.* **5**, 438 (2009).

²R. Yu, W. Zhang, H.-J. Zhang, S.-C. Zhang, X. Dai, and Z. Fang, *Science* **329**, 61 (2010).

³D.-X. Qu, Y. S. Hor, J. Xiong, R. J. Cava, and N. P. Ong, *Science* **329**, 821 (2010).

⁴C. Z. Chang, J. S. Zhang, X. Feng, J. Shen, Z. C. Zhang, M. H. Guo, K. Li, Y. B. Ou, P. Wei, L. L. Wang, Z. Q. Ji, Y. Feng, S. H. Ji, X. Chen, J. F. Jia, X. Dai, Z. Fang, S. C. Zhang, K. He, Y. Y. Wang, L. Lu, X. C. Ma, and Q. K. Xue, *Science* **340**, 167 (2013).

⁵F. Cheng, *Solid State Commun.* **152**, 933 (2012).

⁶V. A. Kulbachinskii, P. V. Gurin, P. M. Tarasov, A. B. Davydov, Y. A. Danilov, and O. V. Vikhrova, *Low Temp. Phys.* **33**, 174 (2007).

⁷S. Mondal, D. Sen, K. Sengupta, and R. Shankar, *Phys. Rev. B* **82**, 045120 (2010).

- ⁸G. Rosenberg and M. Franz, *Phys. Rev. B* **85**, 195119 (2012).
- ⁹Z.-G. Fu, P. Zhang, Z. Wang, and S.-S. Li, *J. Phys.: Condens. Matter* **24**, 145502 (2012).
- ¹⁰T. Habe and Y. Asano, *Phys. Rev. B* **85**, 195325 (2012).
- ¹¹M. S. Foster, *Phys. Rev. B* **85**, 085122 (2012).
- ¹²Y. L. Chen, J. H. Chu, J. G. Analytis, Z. K. Liu, K. Igarashi, H. H. Kuo, X. L. Qi, S. K. Mo, R. G. Moore, D. H. Lu, M. Hashimoto, T. Sasagawa, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z. X. Shen, *Science* **329**, 659 (2010).
- ¹³C. Niu, Y. Dai, M. Guo, W. Wei, Y. Ma, and B. Huang, *Appl. Phys. Lett.* **98**, 252502 (2011).
- ¹⁴T. D. Anh, J. Choi, Y. Shin, S. Cho, H.-M. Park, W. Kim, C. Hwang, and D. D. Duc, *J. Korean Phys. Soc.* **61**, 1675 (2012).
- ¹⁵J. L. Cui, L. D. Mao, W. Yang, X. B. Xu, D. Y. Chen, and W. J. Xiu, *J. Solid State Chem.* **180**, 3583 (2007).
- ¹⁶J. Bludská, I. Jakubec, C. Drasar, P. Lostak, and J. Horak, *Philos. Mag.* **87**, 325 (2007).
- ¹⁷Z.-G. Chen, G. Han, L. Yang, L. Cheng, and J. Zou, *Prog. Nat. Sci.* **22**, 535 (2012).
- ¹⁸V. A. Kulbachinskii, A. Y. Kaminskii, K. Kindo, Y. Narumi, K. Suga, P. Lostak, and P. Svanda, *Physica B* **311**, 292 (2002).
- ¹⁹D. West, Y. Y. Sun, S. B. Zhang, T. Zhang, X. Ma, P. Cheng, Y. Y. Zhang, X. Chen, J. F. Jia, and Q. K. Xue, *Phys. Rev. B* **85**, 081305 (2012).
- ²⁰J. J. Cha, J. R. Williams, D. Kong, S. Meister, H. Peng, A. J. Bestwick, P. Gallagher, D. Goldhaber-Gordon, and Y. Cui, *Nano Lett.* **10**, 1076 (2010).
- ²¹V. A. Kulbachinskii, P. M. Tarasov, and E. Bruck, *Physica B* **368**, 32 (2005).
- ²²V. A. Kulbachinskii, P. M. Tarasov, and E. Bruck, *J. Exp. Theor. Phys.* **101**, 528 (2005).
- ²³P. P. J. Haazen, J. B. Laloe, T. J. Nummy, H. J. M. Swagten, P. Jarillo-Herrero, D. Heiman, and J. S. Moodera, *Appl. Phys. Lett.* **100**, 082404 (2012).
- ²⁴J. Choi, S. Choi, Y. Park, H. M. Park, H. W. Lee, B. C. Woo, and S. Cho, *Phys. Status Solidi B* **241**, 1541 (2004).
- ²⁵J. Choi, H. W. Lee, B. S. Kim, S. Choi, J. H. Song, and S. L. Cho, *J. Appl. Phys.* **97**, 10D324 (2005).
- ²⁶J. W. G. Bos, M. Lee, E. Morosan, H. W. Zandbergen, W. L. Lee, N. P. Ong, and R. J. Cava, *Phys. Rev. B* **74**, 184429 (2006).
- ²⁷J. S. Dyck, P. Hajek, P. Losit'ak, and C. Uher, *Phys. Rev. B* **65**, 115212 (2002).
- ²⁸H. B. Zhang, H. L. Yu, D. H. Bao, S. W. Li, C. X. Wang, and G. W. Yang, *Adv. Mater.* **24**, 132 (2012).
- ²⁹Y. S. Hor, P. Roushan, H. Beidenkopf, J. Seo, D. Qu, J. G. Checkelsky, L. A. Wray, D. Hsieh, Y. Xia, S. Y. Xu, D. Qian, M. Z. Hasan, N. P. Ong, A. Yazdani, and R. J. Cava, *Phys. Rev. B* **81**, 195203 (2010).
- ³⁰L. Cheng, Z.-G. Chen, S. Ma, Z.-d. Zhang, Y. Wang, H.-Y. Xu, L. Yang, G. Han, K. Jack, G. Lu, and J. Zou, *J. Am. Chem. Soc.* **134**, 18920 (2012).
- ³¹F. Xiu, L. He, Y. Wang, L. Cheng, L.-T. Chang, M. Lang, G. Huang, X. Kou, Y. Zhou, X. Jiang, Z.-G. Chen, J. Zou, A. Shailos, and K. L. Wang, *Nat. Nano.* **6**, 216 (2011).
- ³²L. Fu, C. L. Kane, and E. J. Mele, *Phys. Rev. Lett.* **98**, 106803 (2007).
- ³³G. Brumfiel, *Nature* **466**, 310 (2010).
- ³⁴M. Franz, *Nature Mater.* **9**, 536 (2010).
- ³⁵J. Moore, *Nat. Phys.* **5**, 378 (2009).
- ³⁶H. Peng, K. Lai, D. Kong, S. Meister, Y. Chen, X.-L. Qi, S.-C. Zhang, Z.-X. Shen, and Y. Cui, *Nature Mater.* **9**, 225 (2010).
- ³⁷W. Dang, H. Peng, H. Li, P. Wang, and Z. Liu, *Nano Lett.* **10**, 2870 (2010).
- ³⁸H. Peng, W. Dang, J. Cao, Y. Chen, D. Wu, W. Zheng, H. Li, Z.-X. Shen, and Z. Liu, *Nat. Chem.* **4**, 281 (2012).
- ³⁹Y. Wang, F. Xiu, L. Cheng, L. He, M. Lang, J. Tang, X. Kou, X. Yu, X. Jiang, Z. Chen, J. Zou, and K. L. Wang, *Nano Lett.* **12**, 1170 (2012).
- ⁴⁰R. J. Mehta, Y. Zhang, C. Karthik, B. Singh, R. W. Siegel, T. Borca-Tasciuc, and G. Ramanath, *Nature Mater.* **11**, 233 (2012).
- ⁴¹K. J. Koski, J. J. Cha, B. W. Reed, C. D. Wessells, D. Kong, and Y. Cui, *J. Am. Chem. Soc.* **134**, 7584 (2012).
- ⁴²K. J. Koski, C. D. Wessells, B. W. Reed, J. J. Cha, D. Kong, and Y. Cui, *J. Am. Chem. Soc.* **134**, 13773 (2012).
- ⁴³Z.-G. Chen, J. Zou, F. Li, G. Liu, D.-M. Tang, D. Li, C. Liu, X. Ma, H.-M. Cheng, G. Q. Lu, and Z. Zhang, *Adv. Funct. Mater.* **17**, 3371 (2007).
- ⁴⁴E. J. Menke, M. A. Brown, Q. Li, J. C. Hemminger, and R. M. Penner, *Langmuir* **22**, 10564 (2006).
- ⁴⁵H. Bando, K. Koizumi, Y. Oikawa, K. Daikohara, V. A. Kulbachinskii, and H. Ozaki, *J. Phys. Condens. Matter* **12**, 5607 (2000).
- ⁴⁶T. Kondo, Y. Nakashima, Y. Ota, Y. Ishida, W. Malaeb, K. Okazaki, S. Shin, M. Kriener, S. Sasaki, K. Segawa, and Y. Ando, *Phys. Rev. Lett.* **110**, 217601 (2013).
- ⁴⁷Y. S. Hor, A. J. Williams, J. G. Checkelsky, P. Roushan, J. Seo, Q. Xu, H. W. Zandbergen, A. Yazdani, N. P. Ong, and R. J. Cava, *Phys. Rev. Lett.* **104**, 057001 (2010).
- ⁴⁸B. J. Lawson, Y. S. Hor, and L. Li, *Phys. Rev. Lett.* **109**, 226406 (2012).
- ⁴⁹S. Sasaki, M. Kriener, K. Segawa, K. Yada, Y. Tanaka, M. Sato, and Y. Ando, *Phys. Rev. Lett.* **107**, 217001 (2011).
- ⁵⁰S. J. Blundell, *Magnetism of Condensed Matter* (Oxford University Press, 2001), p. 256.