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Ferromagnetism in thin-film Cr-doped topological insulator Bi_2Se_3

P. P. J. Haazen,[1,2,a)] J.-B. Laloë,[1] T. J. Nummy,[3] H. J. M. Swagten,[2] P. Jarillo-Herrero,[4] D. Heiman,[3] and J. S. Moodera[1,4]
[1]*Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*
[2]*Department of Applied Physics, Center for NanoMaterials and COBRA Research Institute, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[3]*Department of Physics, Northeastern University, Boston, Massachusetts 02115, USA*
[4]*Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

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We report on the observation of ferromagnetism in epitaxial thin films of the topological insulator compound Bi_2Se_3 with chromium doping. The structural, magnetic, and magnetoelectrical properties of Bi_2Se_3 were investigated for Cr concentrations up to 10%. For a Cr content up to ~5% the films are of good crystalline quality, with the lattice parameter *a* decreasing and the lattice parameter *c* increasing with increasing Cr concentration. The Curie temperature reached a maximum $T_C = 20$ K for 5.2% Cr. Well-defined ferromagnetic hysteresis in the magnetization and in the magnetoresistance was also observed in these films. © *2012 American Institute of Physics*. [doi:10.1063/1.3688043]

Topological insulators (TIs) are materials with a bulk band gap but have a conducting surface state.[1–4] This surface state has two special properties: it exhibits a relativistic-like linear energy-momentum dispersion, analogous to graphene, and its conducting character is protected by time-reversal symmetry. The latter confers on the surface state its topological protection, i.e., the surface state remains gapless even in the presence of moderate disorder. The unique geometry, non-degenerate band structure, and topological characteristics of the TI surface states have generated extraordinary interest in the physics community and have led, together with graphene, to the emergence of a paradigm of "relativistic" condensed matter physics.[2–4]

Among the various early discovered TI materials based on Bi compounds,[1,5–8] Bi_2Se_3 is one of the most promising candidates for electronic applications: it has a single Dirac cone in the Brillouin zone and a relatively large bulk energy gap of 300 meV, which may be sufficient for room temperature applications.[5,6,8] TIs may also be of interest for future spintronics technology since the helical Dirac surface states may potentially be used to carry spin currents with little heat dissipation.[2–4,9] Additional spin functionality may occur with the development of ferromagnetism in Bi_2Se_3, which is interesting in itself, because the combination of magnetism with TIs can lead to exotic phenomena, such as the point-charge-induced magnetic monopole and topological contributions to the Faraday and Kerr magneto-optical effects.[10] Ferromagnetism has been found in several doped TIs: in V-, Cr-, and Mn-doped single crystals of Sb_2Te_3,[11–15] Fe- and Mn-doped single crystals of Bi_2Te_3,[15–17] and Fe-doped single crystals of Bi_2Se_3,[18] although the latter report suggests that the magnetism may be partly induced by inclusions and may not be due to ferromagnetism of the bulk matrix. Mn-doped single crystals of Bi_2Se_3 were found to have a spin-glass behavior,[19] and a recent report found antiferromagnetism in highly Cr-doped (15%) Bi_2Se_3 bulk crystals.[20] Low temperature MBE growth has the potential of allowing for higher doping concentrations, a fact that was exploited in thin films of Cr-Sb_2Te_3, in which a Curie temperature of 190 K was found.[21] Our present letter focuses on ferromagnetism in thin films of Cr-Bi_2Se_3.

In most conventional diluted magnetic semiconductors it is understood that the exchange interaction requires the presence of free carriers, typically in concentrations of the order of 10^{19}–10^{20} cm^{-3}.[22] This range of carrier concentration is undesired in TIs since the contribution to the conduction from the bulk may then dominate over the surface contribution. Hence, a ferromagnetic TI with low bulk conduction should not depend on this interaction. Recently, it has been predicted that materials such as Cr-doped Bi_2Se_3 could be magnetic.[23] In this material, the carrier concentration is expected to be low since Cr substitutes for Bi without adding carriers. In Cr-doped Bi_2Se_3, the exchange interaction is mediated by band electrons, in contrast to conventional diluted magnetic semiconductors, and in the ultrathin limit it is expected to give rise to the quantum anomalous Hall effect (QAHE): a quantized Hall conductance in the absence of an external magnetic field when the chemical potential is tuned in the bulk gap.[23]

In this letter we report on the observation of ferromagnetism in Cr-doped Bi_2Se_3 films. Bi, Se, and Cr were co-evaporated under ultra high vacuum conditions by molecular beam epitaxy (MBE). The MBE chamber had a base pressure of 5×10^{-10} Torr, and samples were grown at 220 °C on Si(111) substrates. The Cr concentrations reported below refer to the total atomic Cr percentage $Cr_x(Bi_2Se_3)_{1-x}$ in the range x = 0–10%, as measured by energy dispersive x-ray analysis. The films with low doping are highly textured, with the *c*-axis perpendicular to the surface plane, as shown in Fig. 1 by the strong (00*l*) x-ray diffraction (XRD) peaks. For samples with $x \geq 5.9\%$, no XRD peaks from the crystalline Cr-Bi_2Se_3 phase are observed. The *c* lattice parameter increases as function of Cr doping: from 28.68 ± 0.02 Å to 28.9 ± 0.1 Å for a film with x = 5.2%.

a)Electronic mail: P.P.J.Haazen@student.tue.nl.

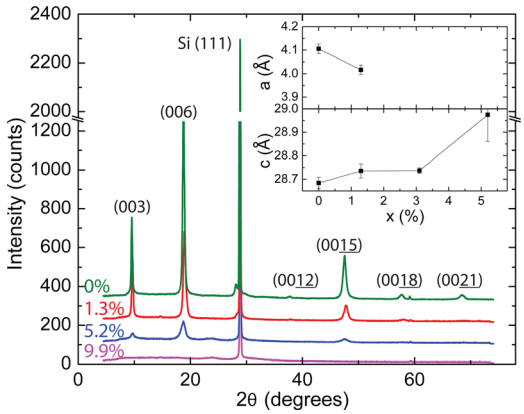

FIG. 1. (Color online) X-ray diffraction scans of thin film samples of Cr-Bi_2Se_3 with various atomic percentages of Cr. Inset: lattice parameters as function of Cr concentration x.

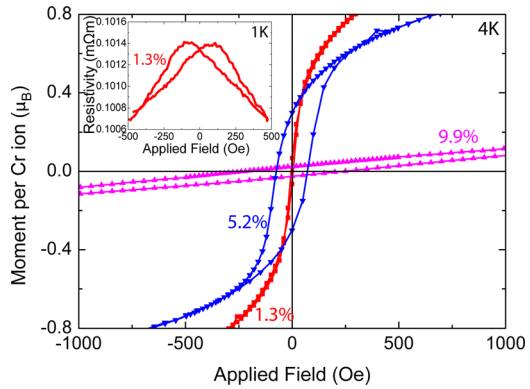

FIG. 2. (Color online) Magnetic moment per Cr ion as a function of applied magnetic field at $T = 4\,K$. Inset: MR signal in a sample with $x = 1.3\%$ at $T = 1\,K$, showing a clear hysteresis.

The crystal quality deteriorates with increasing Cr concentration. However, at low concentrations the samples are highly crystalline: in low-x samples, $x \leq 1.3\%$, a clear six-fold periodicity was observed upon in-plane rotation about the (0120) diffraction peak, indicating that these films are close to being epitaxial. In this doping regime, rocking curves on the Bi_2Se_3 peak have a FWHM of 3.9°. Samples with higher Cr concentrations are more polycrystalline, and their rocking curves have a FWHM up to 6.8° for $x = 5.2\%$, but remain highly textured as can be seen in Fig. 1.

From the (01$\underline{2}$0) peak, which can be found by offsetting the x-ray source and detector from the original Bragg-Brentano geometry that was used for the scans of Fig. 1, we determined that the *a* lattice parameter decreased from 4.11 ± 0.02 Å for an undoped film to 4.02 ± 0.02 Å for $x = 1.3\%$ Cr doping. Because of the loss of Bi_2Se_3 crystallinity, the (01$\underline{2}$0) peak was not detected in samples with $x > 1.3\%$, so the change of the lattice parameter *a* could not be determined for these samples. The increase in the *c* lattice parameter is not expected if only the substitution of Bi by Cr is considered, because the ionic radius of Cr is smaller. In copper-doped Bi_2Se_3, the role of chromium is dual; it is both substituting for the bismuth in the lattice and incorporated inside the Van der Waals gap of the crystal structure between quintuple layers.[24] A similar mechanism can cause the increase of the *c*-axis in the Cr-doped films, especially at high doping concentrations. Although the behavior of Cu can be controlled by the growth conditions, the increase in lattice parameter *c*, 0.07–0.09 Å for ~2% Cu doping, is similar to what we observe for Cr-doping, which is expected because the ionic radii of Cu and Cr are of similar magnitude. Furthermore, at high concentrations, interstitial defects could play a significant role in explaining the increase in the *c* lattice parameter.

The in-plane magnetic properties of the samples were measured with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design XL-5). Figure 2 shows the low-temperature magnetic moment normalized per Cr ion as a function of applied field. A clear hysteresis loop is visible for $x = 5.2\%$ at $T = 4\,K$. For lower concentrations (e.g., $x = 1.3\%$), the hysteresis is almost negligible at $T = 4\,K$, but it is present at lower temperatures. This can also be seen in the magneto-resistance (MR) signal as shown in the inset of Fig. 2, measured on a Hall-bar patterned film with $x = 1.3\%$ Cr at $T = 1\,K$. Although the coercive field is negligibly small at $T = 4\,K$ (as determined by the SQUID and MR), at $T = 1\,K$ it is approximately $H = 80$ Oe. Hence, even our low Cr-doped, highly crystalline films show clear ferromagnetic behavior. Furthermore, it confirms that the magnetism originates from the entire film instead of magnetic clusters since transport measurements are less sensitive to isolated ferromagnetic particles. The resistivity of low-doped films is $\sim 5\times$ higher than undoped films grown in our MBE apparatus.[25] The carrier concentration is dominated by Se vacancies, and the addition of Cr appears to have a negligible effect on the carrier concentration.[26] Instead, the increase in resistivity is attributed to a decrease in mobility due to the existence of grain boundaries in the deteriorating crystal structure.

The measured magnetic saturation moment per chromium ion is $\mu/\mu_B \sim 2$ for the lowest doped films, whereas $\mu/\mu_B = 3$ is expected in a system where all of the chromium is fully aligned in the Cr^{3+} state and assuming a total quenching of the orbital moment. This discrepancy points to the fact that not all Cr contributes to the ferromagnetism (by, for example, the formation of an antiferromagnetic substance such as Cr or CrSe) or to the Cr being in a different valence state than the expected Cr^{3+}. For high concentrations ($x > 5.2\%$), the moment per Cr drops significantly. This trend can also be seen in the temperature dependence of the magnetization, normalized per Cr ion, at an applied field of $H = 100$ Oe, as shown in Fig. 3. With increasing Cr concentration, the Curie temperature increases first until it reaches $T_C \sim 20\,K$ for $x = 5.2\%$ then decreases for higher x values. The significant drop of the magnetic moment per Cr ion for $x > 5.2\%$ coincides with the loss of the Cr-Bi_2Se_3 crystallinity. A similar behavior can be seen in the inset of Fig. 3, where we consider the saturation moment per Cr atom as a function of Cr content at $T = 4\,K$, which decreases sharply beyond $x = 5.2\%$. This strong dependence is further evidence that the magnetism indeed originates from the crystalline Cr-Bi_2Se_3 phase. Up to $x = 5.2\%$, the Cr substitutes mainly for the Bi, resulting in an increase in magnetic moment and Curie temperature. Beyond that concentration, the added Cr breaks up the long range crystalline order and consequently

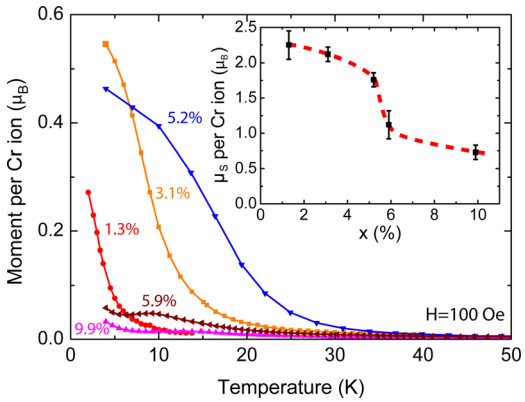

FIG. 3. (Color online) Magnetic moment per Cr ion in Bohr magneton, as a function of temperature. The inset shows the magnetic saturation moment μ_S per Cr ion as a function of Cr content x. The dashed curve is a guide to the eye.

the ferromagnetic order ceases to increase. Thus, the magnetism is related to the doping concentration and resulting crystallinity, and other magnetic impurities are unlikely. Cr clustering would also not give rise to ferromagnetism since Cr is antiferromagnetic as are Cr_xSe_y compounds. This was also experimentally verified by growing Cr_xSe_y films which were found to have no magnetic signature.

As discussed in the introduction, electrostatic gating of TI thin films[27,28] is of interest because it might drive the system into the QAHE state. The present 70 nm thick Cr-Bi_2Se_3 films are too thick to gate them effectively, and the coupling between the top and bottom surfaces is too small to observe the QAHE. Yu *et al.*[23] predicted that the Curie temperature drops only by about 10 K in thinner films due to finite-size effects. Our results therefore indicate that ultra-thin films of Cr-Bi_2Se_3 would still have a Curie temperature in a temperature range easily obtainable in experiments and would therefore be excellent candidates for QAHE and other magnetism/TI experiments.

In summary, we have studied ferromagnetism in MBE-grown epitaxial Cr-doped Bi_2Se_3 thin films and investigated their dependence on Cr concentration. The highest T_C of about 20 K can be achieved by a doping of 5% Cr. The magnetic moment and Curie temperature depend strongly on the Cr concentration. Several observations point to the intrinsic nature of the ferromagnetism in Cr-Bi_2Se_3. These include the strong magnetoelectrical coupling in the MR, the intrinsic antiferromagnetism of Cr and CrSe, and the simultaneous degradation of the ferromagnetism and the Bi_2Se_3 crystallinity. However, further investigation is required to establish the exact mechanism for ferromagnetism in these films and the possibility to observe the QAHE.

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[1]D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature **452**, 970 (2008).
[2]X. L. Qi and S. C. Zhang, Physics Today **63**(1), 33 (2010).
[3]J. E. Moore, Nature **464**, 194 (2010).
[4]M. Z. Hasan and C. L. Kane, Rev. Mod. Phys. **82**, 3045 (2010).
[5]Y. Xia, D. Qian, D. Hsieh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature Phys. **5**, 398 (2009).
[6]H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Nature Phys. **5**, 438 (2009).
[7]Y. L. Chen, J. G. Analytis, J.-H. Chu, Z. K. Liu, S.-K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z.-X. Shen, Science **325**, 178 (2009).
[8]D. Hsieh, Y. Xia, D. Qian, L. Wray, J. H. Dil, F. Meier, J. Osterwalder, L. Patthey, J. G. Checkelsky, N. P. Ong, A. V. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature **460**, 1101 (2009).
[9]P. Roushan, J. Seo, C. V. Parker, Y. S. Hor, D. Hsieh, D. Qian, A. Richardella, M. Hasan, R. J. Cava, and A. Yazdani, Nature **460**, 1106 (2009).
[10]X.-L. Qi, T. L. Hughes, and S.-C. Zhang, Phys. Rev. B **78**, 195424 (2008).
[11]J. S. Dyck, W. Chen, P. Hájek, P. Lošt'ák, and C. Uher, Physica B **312–313**, 820 (2002).
[12]J. S. Dyck, P. Hájek, P. Lošt'ák, and C. Uher, Phys. Rev. B **65**, 115212 (2002).
[13]J. S. Dyck, C. Drasar, P. Lošt'ák, and C. Uher, Phys. Rev. B **71**, 115214 (2005).
[14]J. S. Dyck, P. Svanda, P. Lošt'ák, J. Horak, W. Chen, and C. Uher, J. Appl. Phys. **94**, 7631 (2003).
[15]J. Choi, S. Choi, J. Choi, Y. Park, H. Park, H. Lee, B. Woo, and S. Cho, Phys. Status Solidi B **241**, 1541 (2004).
[16]Y. 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).
[17]V. A. Kulbachinskii, A. Y. Kaminskii, K. Kindo, Y. Narumi, K. Suga, P. Lostak, and P. Svanda, Physica B: Condens. Matter. **311**, 292 (2002).
[18]Y. 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. Hus-sain, and Z. X. Shen, Science **329**, 659 (2010).
[19]J. Choi, H.-W. Lee, B.-S. Kim, H. Park, S. Choi, S. Hong, and S. Cho, J. Magn. Magn. Mater. **304**, e164 (2006).
[20]Y. H. Choi, N. H. Jo, K. J. Lee, J. B. Yoon, C. Y. You, and M. H. Jung, J. Appl. Phys. **109**, 07E312 (2011).
[21]Z. Zhou, Y.-J. Chien, and C. Uher, Phys. Rev. B **74**, 224418 (2006).
[22]T. Dietl, Semicond. Sci. Technol. **17**, 377 (2002).
[23]R. Yu, W. Zhang, H.-J. Zhang, S.-C. Zhang, X. Dai, and Z. Fang, Science **329**, 61 (2010).
[24]Y. 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).
[25]H. Steinberg, J.-B. Laloë, V. Fatemi, J. S. Moodera, and P. Jarillo-Herrero, Phys. Rev. B **84**, 233101 (2011).
[26]B. A. Assaf, T. Cardinal, P. Wei, F. Katmis, J. S. Moodera, and D. Heiman, "Modified electrical transport probe design for standard magnetometer" (unpublished).
[27]H. Steinberg, D. R Gardner, Y. S. Lee, and P. Jarillo-Herrero, Nano Lett. **10**, 5032 (2010).
[28]J. Checkelsky, Y. Hor, R. Cava, and N. Ong, e-print arXiv:1003.3883v1.