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Origin of the temperature dependence of the energy gap in Cr-doped Bi_2Se_3

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Recent progress in impurity-doped topological insulators has shown that the gap at the Dirac point shrinks with reducing temperature. This is an obstacle for experimental realization of the quantum anomalous Hall effect at higher temperature due to the requirement of a larger energy gap. In order to solve this puzzle, we study the gap at the Dirac point by performing temperature-dependent photoemission spectroscopy and X-ray diffraction experiments in Cr-doped Bi_2Se_3 . Our valence band photoemission study revealed that the gap alters with temperature due to residual gas condensation on the sample surface with cooling. Residual gas on the sample surface creates an electron doping effect that modifies the chemical potential of the system resulting in the change of the gap size with variable temperature. Furthermore, such electron doping can weaken the ferromagnetism and lead to a bulk band contribution in the transport measurements. Therefore, such effects can hinder the existence of the quantum anomalous Hall state at higher temperatures. Hence, this work can pave the way for future studies towards a high-temperature quantum anomalous Hall effect.

Introduction

Topological insulators (TIs) attract scientists due to their distinct electronic structure and their potential to revolutionize information technology. They are insulators in the bulk but possess very special metallic surfaces due to strong spin-orbit coupling.^{1–4} Surface electrons of TIs obey the massless Dirac equation where the electron energy disperses linearly with respect to its momentum. This forms the Dirac cone in momentum space with a special crossover singularity known as the Dirac point (DP).⁴ On the surface of TIs, time reversal symmetry (TRS) constrains the momentum and spin of electrons locked perpendicularly to each other leading to the absence of backscattering. Hence, surface states of TIs are topologically protected from non-magnetic impurity scattering and sample imperfections.^{4–6}

In contrast, a long-range magnetic order can open a surface energy gap at the DP by breaking the time reversal symmetry (TRS).^{7–9} The gap has been experimentally observed in various transition metal doped Bi_2Se_3 topological insulators by angle-resolved photoemission spectroscopy (ARPES).^{9–12} Magnetic TIs with broken TRS are of great interest for being a new avenue to observe the quantum anomalous Hall effect (QAHE).^{13,33–35} Growing interest in magnetic TIs, however, has brought about

several unexpected results. For example, recent studies on Cr and Mn-doped Bi_2Se_3 revealed that the Dirac cone can be gapped without a need for magnetization.^{14–18,21} This gap at the DP was attributed to scattering of Dirac electrons by the impurity-induced states located at and around the DP.^{19–21} In addition, the gap size in $\text{Bi}_{2-x}\text{Cr}_x\text{Se}_3$ (for $x > 0$) depends on the chemical potential, which can be controlled by incorporating Mg into the bulk of the sample.¹⁴ Another intriguing realization is the temperature dependence of the gap.^{14,23} For example, the 70 meV gap measured at room temperature (RT) for a $\text{Bi}_{1.96}\text{Cr}_{0.04}\text{Se}_3$ sample almost vanishes at 80 K.¹⁴ The physics behind the temperature dependence of the gap has not been investigated and is still waiting to be explained. Here, we aim to solve this puzzle in Cr-doped Bi_2Se_3 ($\text{Bi}_{2-x}\text{Cr}_x\text{Se}_3$) by performing temperature-dependent ARPES, X-ray photoemission spectroscopy (XPS), and X-ray diffraction (XRD) experiments. We found that the temperature dependence of the gap arises from the residual gas condensation on the sample surface with sample cooling. The residual gas creates an electron rich surface and modifies the chemical potential of the system resulting in the suppression of the gap at low temperature. The findings in this report can contribute to the understanding of why the QAHE can be observed only at extremely low temperatures in similar systems.

Experiment

Molecular beam epitaxy (MBE) is employed for growing high quality pristine and Cr-doped Bi_2Se_3 thin films on Al_2O_3 (0001) substrates.

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The two-step method is applied by depositing a few-quintuple layers (QL) of the film at 390 K and depositing more at 490 K substrate temperature. The samples were annealed for 10 minutes at 490 K to promote the surface quality of the films. Angle-resolved photoemission spectroscopy and valence band spectra were collected with He I α radiation ($h\nu = 21.2$ eV) and a Scienta SES-100 electron analyzer. Core levels were recorded with Al K α X-rays ($h\nu = 1486.6$ eV). The growth chamber with a base pressure of 1×10^{-9} Torr and the photoemission chamber with a base pressure of 2×10^{-10} Torr were vacuum-interlocked. Hence, photoemission measurements were carried without breaking the vacuum. This experimental setup provides a unique way of monitoring the electronic structure of freshly grown samples.

Results and discussion

The unique electronic structure of Bi₂Se₃ and the impact of Cr-doping on the surface states of Bi₂Se₃ were investigated by means of ARPES. Fig. 1(a) shows the ARPES spectrum of a pristine Bi₂Se₃ film at RT. The gapless and linear dispersion of the surface states constructing the DP at $\Gamma(000)$ and 180 meV binding energy demonstrate the topological insulator character of the Bi₂Se₃ film. In addition, the corresponding energy dispersive curves (EDCs) are presented in Fig. 1(b) in which the gapless feature of the topological surface states is marked with a solid blue line.

Cr-doping has a sudden and dramatic impact on the electronic structure of Bi₂Se₃. First, Cr incorporating into the bulk of Bi₂Se₃ causes broader energy bands that limit the ability to distinguish the surface and the bulk states. Second, it destroys the Dirac-like surface states and opens an energy gap at the DP as shown in Fig. 2(a) for the Bi_{1.84}Cr_{0.16}Se₃ film. Such gap opening at the DP indicates the mass acquisition of the Dirac fermions by breaking TRS and lifting the Kramer's degeneracy. In addition, increasing Cr content from $x = 0.16$ to 0.22 results in a larger energy gap (Fig. 2(b)). The gap is measured from the bottom of the upper surface states to the top of the lower surface states as indicated

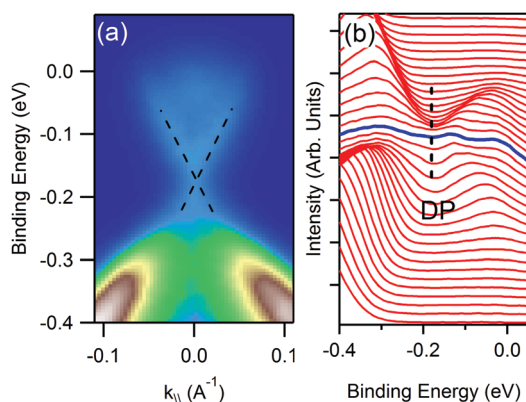


Fig. 1 (a) ARPES energy mapping of Bi₂Se₃ ($x = 0$) at RT and (b) the corresponding energy dispersive curves (EDCs). Dashed black lines in (a) represent the topological surface states of Bi₂Se₃. The spectrum was recorded with 21.2 eV (He I α) photon energy along the Γ - M direction.

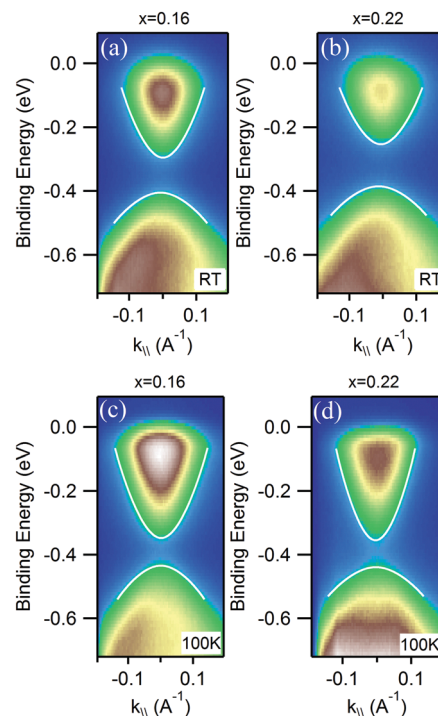


Fig. 2 (a) and (b) are ARPES data at RT for Bi_{1.84}Cr_{0.16}Se₃ ($x = 0.16$) and Bi_{1.78}Cr_{0.22}Se₃ ($x = 0.22$), respectively. (c) and (d) are ARPES energy maps at 100 K for $x = 0.16$ and $x = 0.22$, respectively. Spectra were recorded with 21.2 eV (He I α) photon energy along the Γ - M direction. Solid white lines represent the gap for guiding the eyes.

with white solid parabolas in Fig. 2(a) and (b), and it is measured to be 100 meV for $x = 0.16$ and 130 meV for $x = 0.22$ at RT.

Furthermore, we recorded the electronic structure of Bi_{1.84}Cr_{0.16}Se₃ and Bi_{1.78}Cr_{0.22}Se₃ at 100 K (Fig. 2(c) and (d)). The gap shows temperature dependence and it is measured to be 75 meV at 100 K for both samples. Since Cr-doped Bi₂Se₃ is not magnetic above 35 K,¹⁶ the gap is not expected to fluctuate when the temperature is lowered from RT to 100 K. In addition, measuring the same gap size for different Cr contents at low temperature suggests that the gap size is Cr content independent at 100 K or there are some other factors merging with the decreasing temperature.

A recent study also pointed out that the gap magnitude changes with respect to temperature in TlBi(S_{1-x}Se_x)₂ samples, which is a TI for $x > 0.6$.²³ Increasing the S content leads to the opening of a gap at the DP that shows similar temperature dependence as observed in our samples. TlBi(S_{1-x}Se_x)₂ is a non-magnetic material for all x values. Thus, the dependence of the gap on temperature is attributed to fluctuation or randomness, which can be suppressed at low temperature.²³

There could be several driving factors behind the temperature dependence of the gap. We start our argument by performing a XPS study. Theoretical findings showed that transition metal substitution only occurs with Bi in Bi₂Se₃ and results in opening an energy gap at the DP.²² Therefore, the temperature dependence of the gap may originate from the evolution of the chemical environment with variable temperature. Thus, we recorded the

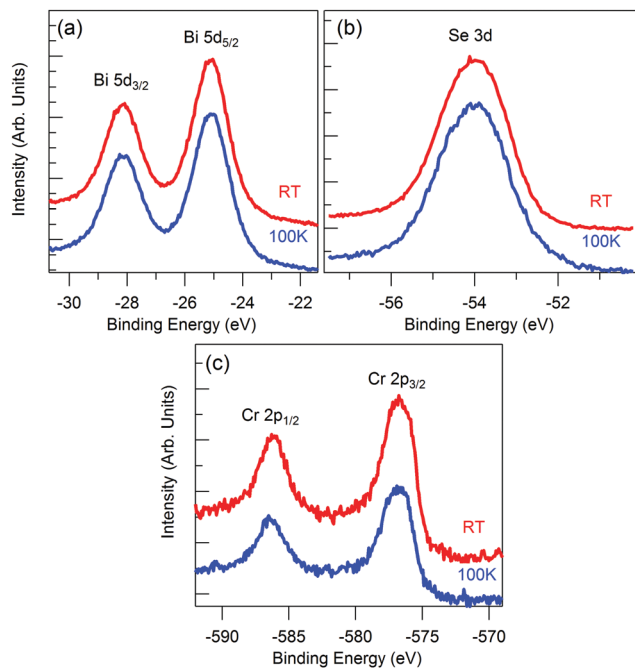


Fig. 3 XPS core level peaks of (a) Bi 5d, (b) Se 3d and (c) Cr 2p obtained from the $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ sample at RT with an Al K α (1458.6 eV) source.

Bi 5d, Se 3d and Cr 2p peaks at RT and 100 K for the $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ sample (Fig. 3). The core-level peaks do not show any prominent difference between the two temperatures except for a 70 meV shift to a higher binding energy with cooling. In addition, at 100 K, Cr 2p_{1/2} and 2p_{3/2} have a binding energy of -586.2 eV and -576.4 eV, respectively. These binding energies correspond to +3 oxidation states indicating that Cr is still in the Bi-lattice site at 100 K. Hence, the chemical structure of $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ is stable with temperature confirming that variation in the chemical environment is not a possible link between the gap size and temperature.

The evolution of the gap with temperature could also arise from the expansion or compression of the *c*-lattice parameter. A recent study revealed that the gap opened at the DP of Bi_2Se_3 can be controlled by strain applied along the surface normal.³² To investigate if this is the case in our samples, we performed XRD on the $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ sample at RT and 100 K (Fig. 4). The *c*-lattice parameter is calculated to be 28.65 ± 0.02 Å at both temperatures indicating the negligible effect of temperature on the *c*-lattice parameter. Therefore, the strain of the *c*-lattice parameter does not play a role in the change of the gap with temperature.

Another origin of the temperature dependence of the gap could be the modification of the chemical potential. Therefore, we studied the valence states of $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ and $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$ at RT and 100 K (Fig. 5(a) and (b)). Energy dispersive curves (EDCs) of $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ recorded at RT consist of only Bi 6p and Se 4p valence band states. We observed one intense peak located at 1.35 eV (A), which is the bonding character of Se 4p. Another prominent peak (B) is located at 2.05 eV (B) dominated by the Bi 6p bonding orbit. Two other peaks located at binding energies

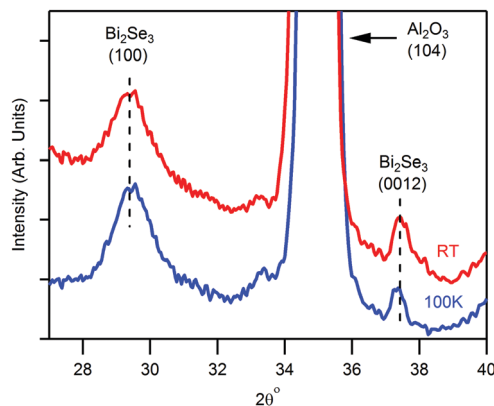


Fig. 4 X-ray diffraction patterns obtained RT (red) and 100 K (blue) for $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ films grown on Al_2O_3 (0001) substrates. Data were collected with Cu K α radiation ($\lambda = 1.5418$ Å). Dashed lines are for guiding the eyes.

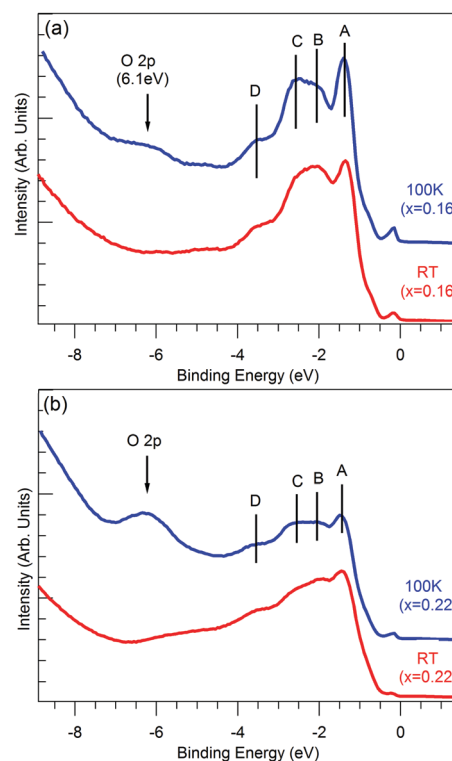


Fig. 5 (a) and (b) are EDCs obtained from $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ and $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$ respectively, at RT (red) and 100 K (blue) at Γ (000) with 21.2 eV (He I α) photon energy. Solid black lines represent the peak positions in the energy scale.

of 2.45 eV (C) and 3.5 eV (D) originate from Bi 6p and Se 4p antibonding orbitals, respectively.^{24,25} Similarly, the EDC of $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$ is also dominated by Se 4p and Bi 6p bonding and antibonding peaks.

At 100 K, however, a peak appears at 6.1 eV marked with an arrow in Fig. 5(a) and (b). The binding energy of the peak corresponds to an oxygen 2p.^{26–28} This arises from the residual gas (CO, CO₂, and H₂O) condensation on the sample surface at low temperature. The condensation of the residual gas has an

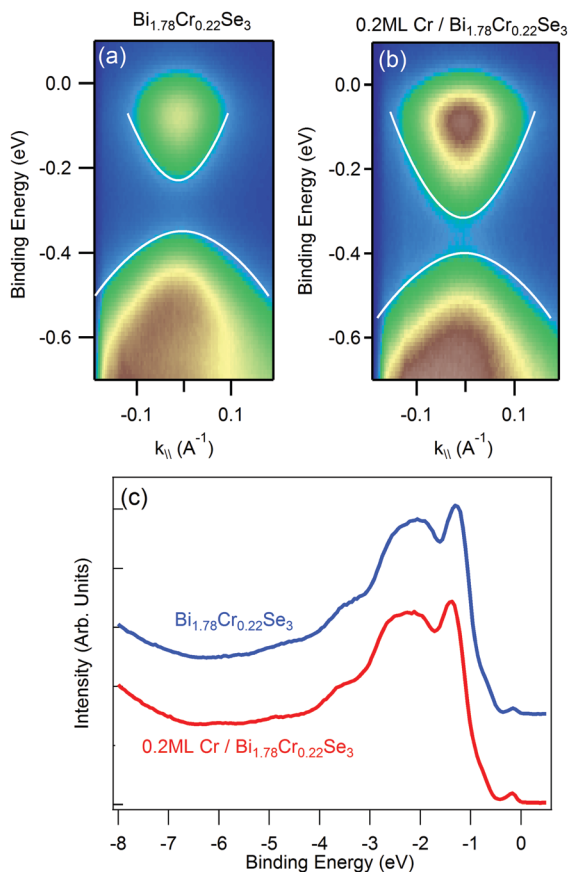


Fig. 6 (a) and (b) ARPES spectra of $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$ and 0.2 ML Cr covered $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$, respectively. (c) EDCs taken at Γ (000) with 21.2 eV (He α) photon energy. The spectra were collected at RT.

electron doping effect on the electronic structure of TIs,^{29–31,40} which is consistent with the shift of our EDCs and XPS peaks to a higher binding energy. Hence, our data confirm the residual gas condensation on the sample surface with cooling. This explains the mechanism behind the temperature dependence of the gap. Such electron doping modifies the chemical potential of the system and consequently the size of the gap as in the case of the Mg doping effect on the electronic structure of $\text{Bi}_{2-x}\text{Cr}_x\text{Se}_3$ (for $x > 0$).¹⁴

For further confirmation, we simulate the electron doping effect by growing extra Cr metal on the surface of $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ (Fig. 6). The valence band spectrum of the undoped sample shifts to higher binding energy upon Cr deposition confirming the more electron-rich surface (Fig. 6(c)). As expected, the gap shrinks from 130 meV to 80 meV as a result of the electron doping effect. Since the spectra were taken at RT before and after the surface deposition of Cr, the EDCs do not show any presence of residual gas on the sample surface. Hence, we provide concrete results to confirm that the gap exhibits temperature dependence due to the modified electronic structure by the electron doping effect of residual gas condensed on the sample surface. Furthermore, the correlation between the size of the gap and the Fermi level can be understood as follows. The gap in the non-magnetic state is attributed to scattering of the Dirac electrons

by the strong impurity resonance states located at and around the DP.^{19–21} This can open a gap at the DP as large as 100 meV, which is compatible with the gap size obtained from our ARPES measurements. The influence of the resonance states depends on the binding energy of the DP and it diminishes with larger energy separation between the DP and the Fermi level.^{38,39} As a consequence of the residual gas condensation on the sample surface, the energy bands shift to higher binding energy. Hence, the size of the gap can shrink as a result of the weakened strength of the resonance states away from the Fermi level.

Conclusion

In conclusion, we present temperature-dependent photoemission and XRD experimental results obtained from $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Se}_3$ and $\text{Bi}_{1.78}\text{Cr}_{0.22}\text{Se}_3$ samples. We found that residual gas condensation on the sample surface with lowering temperature is responsible for the temperature dependence of the gap. Our findings can have a significant importance for enhancing the observation temperature of the QAHE, which is at the center of interest in the TI research area. Recently, QAHE has been observed only in Cr and V-doped $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ in the millikelvin range.^{33,34} One of the essential conditions of the QAHE in TIs is to locate the Fermi level within the bulk band gap to obtain the insulating bulk state and achieve the conduction only by the edge states in transport measurements. Therefore, Bi is added in the Sb_2Te_3 topological insulator to tune the Fermi level inside the bulk band gap where the DP is located.³⁵ However, our spectroscopic studies revealed that air condensation on the sample surface behaves in contrast by pushing the bulk band gap away from the Fermi level, which can obstruct the observation of the QAHE. In addition, early studies showed that the formation of BiO_x layers on the sample surface due to the residual gas affects the electrical properties and the chemical environment of the Bi_2Se_3 .^{36,37} Such formation of the oxide layers on the sample surface buries the topological material under an oxide layer affecting the transport measurement. As a result, such dramatic modification of the electronic structure can play an important role in the absence of the QAHE in Cr-doped Bi_2Se_3 and the observation of the QAHE only in the millikelvin range in the other systems.

Another problem arising due to the modification of the electronic structure is to affect the magnetic properties of the material. In magnetic TIs, TRS is expected to be broken due to the Ruderman–Kittel–Kasuya–Yosida (RKKY) type of ferromagnetism that forms if the gap is near the Fermi level.⁹ However, our spectroscopic study shows a shift of the energy bands to higher binding energy, which could prevent the formation of the RKKY type of ferromagnetism. The RKKY interaction is known as itinerant electron mediated spin interaction between two magnetic impurities when $\lambda_f = 1/k_f$ is larger than the distance between them (where λ_f and k_f are Fermi wavelength and Fermi wavevector, respectively). Therefore, an energy gap can open at the DP when the Dirac fermions are coupled ferromagnetically. Furthermore, the ferromagnetic transition temperature (T_c) is given as $k_B T_c = [(S_0(S_0 + 1)a_0^2 y) / (6\pi\hbar^2 v_f^2)] J_z^2 (E_c - E_f)$ where E_f is the Fermi energy,

E_c is the cut off energy, S_0 is the saturation spin value of each magnetic impurity, a_0 is the lattice constant and J_z is the coupling parameter.⁴¹ This expression states that T_c increases when the DP shifts to the Fermi level. Hence, electron doping due to the residual gas leads to a lower ferromagnetic transition temperature. Furthermore, modification of the chemical potential due to residual gas adsorption can also have an impact on the electronic structure of the system when the magnetic impurities are deposited on the surface of TIs. It is known that Cr impurities prefer to occupy the Bi-substitutional side in Bi_2Se_3 with +3 oxidation states leading to a net out-of-plane magnetic moment.⁴³ However, Cr changes its oxidation state to +2 if there is electron doping in the system.⁴³ This leads to a non-bulk insulating state which changes the carrier concentration of the system.^{42,43}

These problems, indeed, could be overcome by capping the films before taking the samples out from the ultra-high vacuum chamber for magnetic and transport measurements. Te capping has been widely used for such purposes. However, it is claimed that it has an unfavorable effect on the transport measurements.³⁴ Therefore, capping the sample surface without changing the electronic structure is required in order to achieve the high-temperature QAHE.

Conflicts of interest

There are no conflicts to declare.

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