A Sudden Gap-Closure Cross the Topological Phase Transition in (Bi$_{1-x}$In$_x$)$_2$Se$_3$ Single Crystals

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The phase transition from a topological insulator to a band insulator is studied by angle-resolved photoemission spectroscopy on (Bi$_{1-x}$In$_x$)$_2$Se$_3$ single crystals. The robust surface states and the bulk gap size ($\sim 0.50$ eV) show no significant change upon doping for $x = 0.05$, 0.10 and 0.175. At $x \geq 0.225$, the surface states completely disappear and the bulk gap size increases, suggesting a sudden gap-closure and topological phase transition around $x \sim 0.175-0.225$. We find that the unusual evolution of the bulk gap is mainly the consequence of a combined effect of spin-orbit coupling and interactions upon band hybridization, in which the In 5s orbital plays an important role. Our study provides a new venue to investigate the topological phase transition induced by non-magnetic impurities.

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Topological insulators, principally three-dimensional (3D) topological, have attracted much attention due to their compelling physical properties. In particular, these crystals are a new quantum phase of matter with gapless topological surface states located in a larger bulk gap and protected by time reversal symmetry. The two-dimensional (2D) massless surface states, formed by two opposite spin-polarized states, can carry a dissipationless spin current. In addition, their several-hundred meV bulk energy gap enables the application and exploration of the topological properties at room temperature. Extensive theoretical and experimental work has been carried out on both the robust surface states as well as the topological properties of the bulk bands. This work distinguishes a topological insulator from a “trivial” band insulator. Further, the transition between these two classes of insulators has been proposed to be a 3D topological phase transition (TPT) scenario for a substitution by non-magnetic impurities, which is characterized by four $Z_2$ invariants changing parity. This transition happens when an inversion of the bulk conduction band (CB) and valence band (VB) occurs due to spin-orbit coupling (SOC).

The evolution of the proposed homogeneous 3D TPT induced by non-magnetic impurities is expected to be easily realized in TIBi(Se$_{1-x}$S$_x$)$_2$, where the existence of a critical point between the topological insulator TIBiSe$_2$ and the trivial metal TIBiS$_2$ is observed. Upon doping, an unexpected Dirac gap is observed until the elimination of the surface states occurs. However, the evolution of the bulk bands, which mainly characterize the TPT besides the feature of the surface states are still not clear. Another appropriate system to investigate the TPT induced by non-magnetic impurities is (Bi$_{1-x}$In$_x$)$_2$Se$_3$, which processes an even broader TPT from topological insulator to band insulator. As suggested by transport and photoemission measurements on (Bi$_{1-x}$In$_x$)$_2$Se$_3$ thick films, the TPT from the non-trivial to trivial insulator occurs at $x = 0.06$. However, the measured band structures still cannot determine whether the linear gap-closure mechanism is suitable for this system. To further study the evolution of the bulk bands throughout the phase transition and thus investigate the detailed mechanism of the TPT in (Bi$_{1-x}$In$_x$)$_2$Se$_3$, we have performed systematic high-resolution angle-resolved photoemission spectroscopy (ARPES) measurements on (Bi$_{1-x}$In$_x$)$_2$Se$_3$ single crystals.

In this letter, we report an observation of the phase transition from a topological insulator to a band insulator in (Bi$_{1-x}$In$_x$)$_2$Se$_3$ single crystals with various $x$ values ($x = 0.05$, 0.10, 0.175, 0.225 and 0.30), and present the detailed ARPES studies on the evolution of the surface states and bulk band structures as a function of doping. We demonstrate that the bulk gap size ($\sim 0.50$ eV) shows no significant change in the topologically non-trivial region (i.e., $x = 0.05$, 0.10 and 0.175), instead of a linear gap-closure behavior. It is predicted that the bulk gap suddenly closes at a specific doping level ($\sim$...
0.175–0.225) accompanied by the complete suppression of the surface states. After the TPT, i.e., in the topologically trivial region for \( x = 0.225 \) and 0.30, the bulk gap size increases. The combined effect of both SOC and the non-negligible interactions upon band hybridization is suggested to be the dominant factor in this local phase transition, in which the effect of In 5s orbital could not be simply considered as same as the dominated \( p \) orbital character in most topological insulators \([6, 8, 9, 23]\).

The crystal structure of \((\text{Bi}_{1-x}\text{In}_x)_2\text{Se}_3\) is shown in Fig. 1(a), which has a layered structure along the \( z \) direction. The rhombohedral structure belongs to the \( D_{3d}^1 \) (R3\( \bar{m} \)) space group, and the corresponding schematic bulk Brillouin zone (BZ) is presented in Fig. 1(b). As is shown in Fig. 1(c), well-defined peaks in the photoemission core level spectrum of \( x = 0.05 \) sample demonstrate the high quality of the series of crystals used in this work. One can obtain an insight of the binding energy within \( \sim 20 \) eV below \( E_F \) in the core level spectrum, as shown in the inset of Fig. 1(c). The density of states (DOS) near \( E_F \) originates mainly from the Bi 6\( p \) and In 5\( p \) orbitals, and as well the Se 4\( p \) orbital, which contributes to the states both in the conduction band minimum (CBM) and valence band maximum (VBM) according to the band inversion mechanism in the topologically non-trivial phase. Fig. 1(d) shows the Fermi surface (FS) mapping data of \((\text{Bi}_{1-x}\text{In}_x)_2\text{Se}_3\) \( (x = 0.05) \) around the BZ center as a function of in-plane wave vector.

Fig. 1(a) shows the band dispersion of series of doped samples along the \( \Gamma \)\( M \) direction, indicated via cut 1 in Fig. 1(d). The corresponding second derivative plots are shown in Fig. 2(b). The plots clearly show surface states for \( x \leq 0.175 \), thus indicating a topologically non-trivial region, and an absence of surface states for \( x \geq 0.225 \), thus indicating a topologically trivial region. Additionally, one can see the evolution of the bulk band structures from the figures. The bulk gap is defined as the difference between the CBM and the valley of VB at \( \Gamma \) point for the topologically non-trivial region, and the difference between the CBM and VBM is used for the topologically trivial region. In the topologically non-trivial region, the magnitude of bulk gaps extracted from the second derivative plots reveal binding energies of 0.48, 0.50 and 0.49 eV for \( x = 0.05, 0.10 \) and 0.175, respectively, indicating no significant change upon doping. The valley structure in VB caused by the band hybridization between the CB and VB and determining the non-trivial topological properties, gradually weakens along with the increase of In doping, which demonstrates the decrease of the SOC strength. This origin is quantitatively proven by the momentum of the bending band (\( \delta k \)) around the VBM, as marked by solid arrows in Figure 2. The \( \delta k \)'s are 0.091, 0.073 and 0.060 \( \text{Å}^{-1} \) for \( x = 0.05, 0.10 \) and 0.175, respectively. In the topologically trivial region, where In doping is more than 0.225, the bulk gap size increases and the valley structure vanishes owing to the absence of band inversion. In combination with the evolution of surface states and the bulk band structures, we

**FIG. 1.** (Color online) (a) Crystal structure of \((\text{Bi}_{1-x}\text{In}_x)_2\text{Se}_3\) with repeating Se1-Bi/In-Se2-Bi/In-Se1 quintuple layers. (b) Bulk BZ and its surface projection. (c) Core level photoemission spectrum of \((\text{Bi}_{1-x}\text{In}_x)_2\text{Se}_3\) \( (x = 0.05) \). The inset is zoom in of the valence band from the dashed box. (d) ARPES intensity plot of \((\text{Bi}_{1-x}\text{In}_x)_2\text{Se}_3\) \( (x = 0.05) \) at \( E_F \) as a function of the 2D wave vector. The intensity is obtained by integrating the spectra within \( \pm 15 \) meV with respect to \( E_F \). Cut 1 indicates the \( \bar{\Gamma} \bar{M} \) direction, along which the data are presented in Fig. 2. The white dashed circle is guide to the eyes, served as the FS.

High quality single crystals of \((\text{Bi}_{1-x}\text{In}_x)_2\text{Se}_3\) were grown by slowly cooling a stoichiometric mixture of high purity elements of Bismuth, Indium and Selenium in evacuated quartz tube \([24]\). ARPES measurements were performed at Renmin University of China and Institute of Physics, Chinese Academy of Sciences, with a He-discharge lamp (He-I\( \alpha \) line, \( h\nu = 21.218 \) eV), at 1-cubed
predict that a local phase transition characterized by a sudden gap-closure happens close to \( x \sim 0.175 - 0.225 \). Another noticeable observation is the Dirac point (DP) of surface states moving toward the CBM, thus the difference between them decreases along with the increase of In doping. These can be expected to merge at the critical point.

The complete evolution of the bulk gap is shown in Fig. 3(a). The figure shows the evolution of the bulk gap size has a dramatically transform between \( x = 0.175 \) and \( x = 0.225 \), as shown in the shallow region of Fig. 3(a), suggesting a critical transition. This is in contrast to the mild change for \( x = 0.05, 0.10 \) and 0.175 (defined as negative values to distinguish from that in the topologically trivial phase). After crossing the critical point \( (x_c \sim 0.175 - 0.225) \), a strong increase in the bulk gap size from \( x = 0.225 \) to 0.30 is observed. The TPT characterized by this bulk gap evolution slightly deviates from the linear gap-closure mechanism proposed for the non-magnetic-impurity-induced TPT [3, 12–14]. The deviation manifests that SOC should be not the only determinant of the bulk gap behavior in the topologically non-trivial phase.

As proposed in Ref. [12], the band inversion is induced by SOC for a 3D topological insulator. In the topologically non-trivial region, after turning on the SOC, the CB hybridizes with the VB around \( \Gamma \) point. The reopened bulk gap at \( \Gamma \) point \( (i.e., \) the difference between the CBM and the valley) originates from the combined effect of both SOC and interactions upon band hybridization. The overlap ratio, \( \Delta_S \), between the CB and VB without interactions is, \( \Delta_S = |E_g - E_{SOC}| \), in which \( E_g \) is the energy gap between the CBM and VBM before turning on the SOC, is proportional to the covalent bonding strength within the quintuple layer [25], and \( E_{SOC} \) is the total energy shift of the CB and VB after turning on the SOC, is proportional to the SOC strength. Thus, \( \Delta_S \), which corresponds to the relative strength of SOC, and the band hybridization gap, \( \Delta_H \), which is defined as the indirect gap between the CBM and VBM [as shown in Fig. 2(a)], together mediate the evolution of bulk gap upon doping. In the topologically trivial region, the band hybridization vanishes and so does the band inversion. As a consequence, the increase of the bulk gap size characterizes the decrease of SOC strength upon In doping.

As is schematically illustrated in Fig. 3(b), we estimate \( \Delta_S \) as follows, firstly, extracting the \( \delta k \)'s of the VB, shown as black vertical arrows in Fig. 3(b); then, extrapolating the high energy band dispersion to recover the unperturbed VB, and fitting the valley structure to get the dispersion of the unperturbed CB, shown as red dashed curve and purple solid curve in Fig. 3(b), respectively; finally, shifting the unperturbed CB upward (green dashed curve) to match the crossing points, \( i.e., \) \( \delta k \)'s, between

FIG. 2. (Color online) ARPES intensity plots (a) and the corresponding second derivative plots (b) of \((Bi_{1-x}In_x)_2Se_3\) along \( \bar{\Gamma} \bar{M} \) [cut 1 in Fig. 1(d)] direction, for various In doping. The doping \( x = 0.05, 0.10 \) and 0.175 are in the topologically non-trivial region, while \( x = 0.225 \) and 0.30 are in the topologically trivial region. The CBM, VBM, DP, valley and \( \delta k \)'s are marked by green, blue, red and white dashed lines, and solid arrows, respectively. The red dashed curves which represent bulk bands are guides to the eyes.
FIG. 3. (Color online) (a) The evolution of the bulk gap size at $\bar{\Gamma}$ point. The definition of bulk gap in two phases are shown in the insets. The critical point is within the shallow region. (b) A schematic picture of bulk band structure in band hybridization (left panel) and gap-reopening (right panel) in the topologically non-trivial phase. The $\delta k$’s (black vertical arrows) of VB, unperturbed VB (red dashed curve), unperturbed CB (purple solid curve) and shifted CB (green dashed curve) are indicated to estimate $\Delta_S$. (c) $\Delta_S$ (red solid squares) and $\Delta_H$ (blue open circles) as a function of $x$ in the topologically non-trivial phase. The evolution of the estimated bulk gap, $\Delta_E \approx \lambda \cdot \Delta_S + \Delta_H$ ($\lambda = 0.4$) (green open triangles), upon doping is shown in the inset. (d) The doping dependence of the ratio of the enclosed FS area to the whole BZ.

the unperturbed CB and VB. The energy difference between the extreme values of the red and green dashed curves is defined as $\Delta_S$.

In Fig. 3(c), the evolution of $\Delta_S$ and $\Delta_H$ are plotted as a function of In concentration. They have remarkably different tendencies in the topologically non-trivial phase, in which, upon In doping, $\Delta_S$ decreases monotonically, indicating the reduction of the strength of band inversion, while $\Delta_H$ increases mildly. The mildly increasing gap, $\Delta_H$, implies the significance of the doped In 5s orbital in determining the unusual evolution of bulk gap in the topologically non-trivial phase during the TPT. According to the first-principles calculations of $(\text{Bi}_{1-x}\text{In}_x)\text{Se}_3$ at $x = 0.125$ proposed in Ref. [26], in the topologically trivial region, the CBM is composed of the Bi 6p and In 5s orbitals, in which the DOS of the latter is slightly higher than the former, and the VBM is dominated by the Se 4p orbital. Thus, in the topologically non-trivial region, as the interactions upon band hybridization, which are characterized by $\Delta_H$, are proportional to the DOS within the overlap between the CB and VB, the mildly increasing $\Delta_H$ could be referred to the trend of the DOS within the overlap mediated by the In 5s orbital.

Now, we discuss the possible combination of $\Delta_S$ and $\Delta_H$ in determining the bulk gap size. A reasonable estimation of the bulk gap ($\Delta_E$) using the experimental $\Delta_S$ and $\Delta_H$ values is, $\Delta_E \approx \lambda \cdot \Delta_S + \Delta_H$, in which the factor $\lambda$ characterizes the contribution from the SOC. In the topologically non-trivial region, $\lambda = 0.4$, and in the topologically trivial region, $\lambda = 1.0$. Noticing that $\Delta_H \sim 0.4$ eV and $\Delta_S \sim 0.1-0.2$ eV in the topologically non-trivial region, the gap size is dominated by $\Delta_H$ according to this formula. Thus, even $\Delta_S$ decreases faster along with In doping, the gap size changes slightly [as presented in the inset of Fig. 3(c)] at low In concentrations until the band inversion vanishes. Beyond the critical point, $\Delta_H$ vanishes, thus the SOC strength in the topologically trivial region is directly related to the bulk gap, which is proportional to the In concentration. This scenario can explain our observed gap size evolution, as shown in Fig. 3(a).

Additionally, we estimate the carrier concentration of our samples by calculating the ratio of the enclosed FS area to the whole BZ and present it in Fig. 3(d). As the general character of hole-doped systems, the ratio decreases monotonically with increasing doping, agreeing well with the transport measurements proposed in Ref. [20]. When $x \geq 0.30$, the CB almost disappears, and the
A schematic picture of the band structure evolution during the topologically non-trivial region \((x < x_c)\), the band inversion exists, thus the interactions upon band hybridization and SOC together mediate the bulk gap size. As a result, the bulk gap size shows no significant change upon doping. With the increase of In doping and the decrease of SOC strength, the overlap ratio between the CB and VB decreases. At the critical point \((x = x_c)\), the band hybridization vanishes and so does the band inversion, the bulk gap collapses accompanied by the vanishing of surface states. In the topologically trivial region \((x > x_c)\), the further decreasing SOC strength separates the CB and VB, giving rise to the increase of bulk gap. The DP of surface states is moving toward the CBM with the increase of In doping, and the extrapolated merging point is at the vicinity of \(x_c\). This behavior might result from the reduction of the inverted band overlap ratio between the CB and VB and the different orbital characters of the CBM \((p\ orbital)\) and VBM \((s\ orbital)\).

To summarize, we have performed ARPES experiments on \((\text{Bi}_{1-x}\text{In}_x)_2\text{Se}_3\) single crystals to study the band structure evolution of the TPT induced by non-magnetic impurities. Besides the observation of a complete TPT from topological insulator to band insulator for \(0.05 \leq x \leq 0.30\), a sudden gap-closure behavior cross the phase transition is observed. The combined effect of SOC and interactions upon band hybridization is suggested to be the dominant factor, and the In 5s orbital plays a non-negligible role in mediating the contribution from the latter. Based on the observation, a schematic picture of the band structure throughout the TPT is presented, in which the fact that orbital characters of substituted elements different from that of the parent compounds might be significant.

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