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Photoemission-induced gating of topological insulators

A. A. Kordyuk,[1,2] T. K. Kim,[1] V. B. Zabolotnyy,[1] D. V. Evtushinsky,[1] M. Bauch,[1] C. Hess,[1] B. Büchner,[1] H. Berger,[3] and S. V. Borisenko[1]

[1]*Institute for Solid State Research, IFW-Dresden, P.O. Box 270116, D-01171 Dresden, Germany*

[2]*Institute of Metal Physics of National Academy of Sciences of Ukraine, 03142 Kyiv, Ukraine*

[3]*Institute of Physics of Complex Matter, EPFL, CH-1015 Lausanne, Switzerland*

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The recently discovered topological insulators exhibit topologically protected metallic surface states which are interesting from the fundamental point of view and could be useful for various applications if an appropriate electronic gating can be realized. Our photoemission study of Cu-intercalated Bi_2Se_3 shows that the surface-state occupancy in this material can be tuned by changing the photon energy and understood as a photoemission-induced gating effect. Our finding provides an effective tool to investigate the new physics coming from the topological surface states and suggests intercalation as a recipe for synthesis of a material suitable for electronic applications.

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The conelike dispersion of surface states with a spin-degenerate Dirac point, recently observed in photoemission experiments,[1–3] is now considered as a hallmark of topological insulators.[4–6] In this sense, the compound Bi_2Se_3 with a single Dirac cone in the Brillouin zone[1,2] can be considered as the most elementary in the rapidly growing family of topological insulators.[4] This, together with their easily tunable charge carrier concentration by surface doping[2,3] and realization of superconductivity with Cu intercalation,[10,11] makes the Bi_2Se_3 class of materials the most promising for applications in spintronic and computing technologies.[1–3,7–9] The main obstacle here is that, unlike graphene,[12] the three-dimensional (3D) topological insulators cannot be very easily tuned to the zero-carrier-density regime through standard electrical gating,[1,2] although some successful attempts have already been reported.[13] In this Rapid Communication, using ultralow-temperature synchrotron-based angle-resolved photoemission spectroscopy (ARPES) in a wide photon energy range from $h\nu = 20$ to 110 eV, we report the observation of the photoemission-induced gating of Cu-intercalated Bi_2Se_3. This finding opens the possibility of exploring directly and on the same sample the effect of the surface-state occupancy on the low-energy electronic structure, as well as suggesting intercalation as a recipe for synthesis of topological insulators suitable for electronic applications.

Single crystals of Bi_2Se_3 and $Cu_{0.07}Bi_2Se_3$ were grown using the Bridgman method starting with high-purity Bi, Cu, and Se elements. Samples in the form of rectangles with typical dimensions of $5 \times 5 \times 1$ mm^3 were cut for measurements. According to energy-dispersive X-ray (EDX) analysis, the Bi_2Se_3 samples from different batches show different amounts of Se in the range 1%. The sample we measured by ARPES is characterized by typical[14] metallic in-plane resistivity with $\rho_{10\,K} = 0.3$ mΩ cm and $\rho_{300\,K} = 0.5$ mΩ cm. The Cu-doped crystals, which exhibit a large photoinduced gating effect, have been characterized by EDX analysis as $Cu_{0.07}Bi_2Se_3$. They reveal much higher resistivity, as shown in Fig. 1, with a semiconductor-like upturn at low temperature (see the inset). The out-of-plane resistivity for the Cu-doped samples reveals purely semiconducting behavior, increasing monotonically with decreasing temperature from 10–18 mΩ cm at 300 K up to 7–38 Ω cm at 10 K. It is known[15] that Cu doping of Bi_2Se_3 can be realized in two ways: (1) singly ionized interstitial Cu atoms, which go between Se or Bi layers,[15] act as donors; (2) its substitutional defects on bismuth sites, which carry double negative charge, act as acceptors. Both the composition and resistivity data indicate that Cu, in the studied samples, appears mainly as interstitial atoms. Also, we observe an increase of the electronic occupation of the surface states in $Cu_{0.07}Bi_2Se_3$ compared to Bi_2Se_3, which is consistent with Cu intercalation.

ARPES experiments have been performed at the "1^3" beamline at BESSY, equipped with a SES 4000 analyzer and ^{3}He cryomanipulator with the base temperature on the sample less than 1 K.[16] The data are sumarized in Fig. 2. The presented spectra were recorded along cuts through the center of the Brillouin zone close to the ΓM direction. The band position was reproducible with 20 meV accuracy when measured at 1 K and under 8×10^{-11} mbar pressure on the time scale of the experiment (about 6 h) as well as after keeping the cleaved sample at room temperature and at 2×10^{-10} mbar for 34 h. This reproducibility can be seen even from the data presented. For example, the protocol for recording the spectra for $Cu_{0.07}Bi_2Se_3$ presented in Fig. 2(b) is the following: sample cleavage; +2 h 40 min; 50 eV spectrum; +40 min; 33 eV spectrum; +2 h 40 min; 20 eV spectrum; +1 h; 50 eV spectrum again; +1 h; 100 eV spectrum; +34 h; 30 eV spectrum. One should note that for several Bi_2Se_3 samples measured at higher temperatures (10–30 K) we indeed observe a change in the binding energy of the Dirac point as a function of exposure time, about 30 meV during 20 min, which is in agreement with other reports.[2] However, the spectra are recovered when the position of the light spot on the sample surface is changed.

Figure 2 presents the two key observations: (1) The number of topological charge carriers depends on the excitation energy. (2) This dependence correlates with the total current of photoelectrons. The $h\nu$ dependence of the binding energy of the Dirac point, or, in other words, of the surface-state occupancy, can be seen on the raw ARPES spectra presented

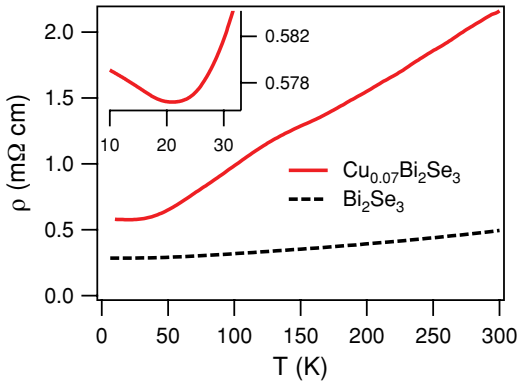

FIG. 1. (Color online) In-plane resistivity of the pure (black dashed line) and Cu intercalated (red solid line) Bi_2Se_3 crystals; the low-temperature region of the later is zoomed in the inset.

in Figs. 2(a) and 2(b) for pure Bi_2Se_3 and a Cu-intercalated sample, respectively. It is summarized in Fig. 2(c) for both samples in terms of the surface-state Fermi surface area. While the effect is weak for the pure crystal, it appears as a clearly detectable step at about 30 eV for $Cu_{0.07}Bi_2Se_3$. The error bars include both the accuracy of the estimation of the Fermi surface area and its detected variations during the experiment.

Taking into account the 2D nature of the surface states, the observation (1) is very surprising. Despite the earlier reported time shift of the surface states that was associated with band bending,[2] absence of essential $h\nu$ dependence of those states has been considered as a proof of their surface origin.[1] Unlike the exposure-time-dependent band bending, the described effect is much larger[2] (150 vs 50 meV) and perfectly reproducible. The observed $h\nu$ dependence also cannot be explained by possible three-dimensionality of the bands because it is monotonic rather then oscillating. Actually, the earlier conclusion about the surface-state origin of the Dirac cone dispersion was based on measurements in the low-excitation-energy range, 19–31 eV. So our result confirms the conclusion about two-dimensionality of the Dirac-cone-forming states on the basis of data from a much wider energy range.

Ruling out the three-dimensionality issue, it is natural to assume that the observed change of the electronic occupation of the surface states is caused by the photoemission process. Due to the discrete energy spectrum of electrons in atoms, the absorption of light and, consequently, the photoemission current from solids, exhibit a stairlike dependence on photon energy, with the steps, known as absorption edges, occurring at the binding energies of the core electrons plus the work

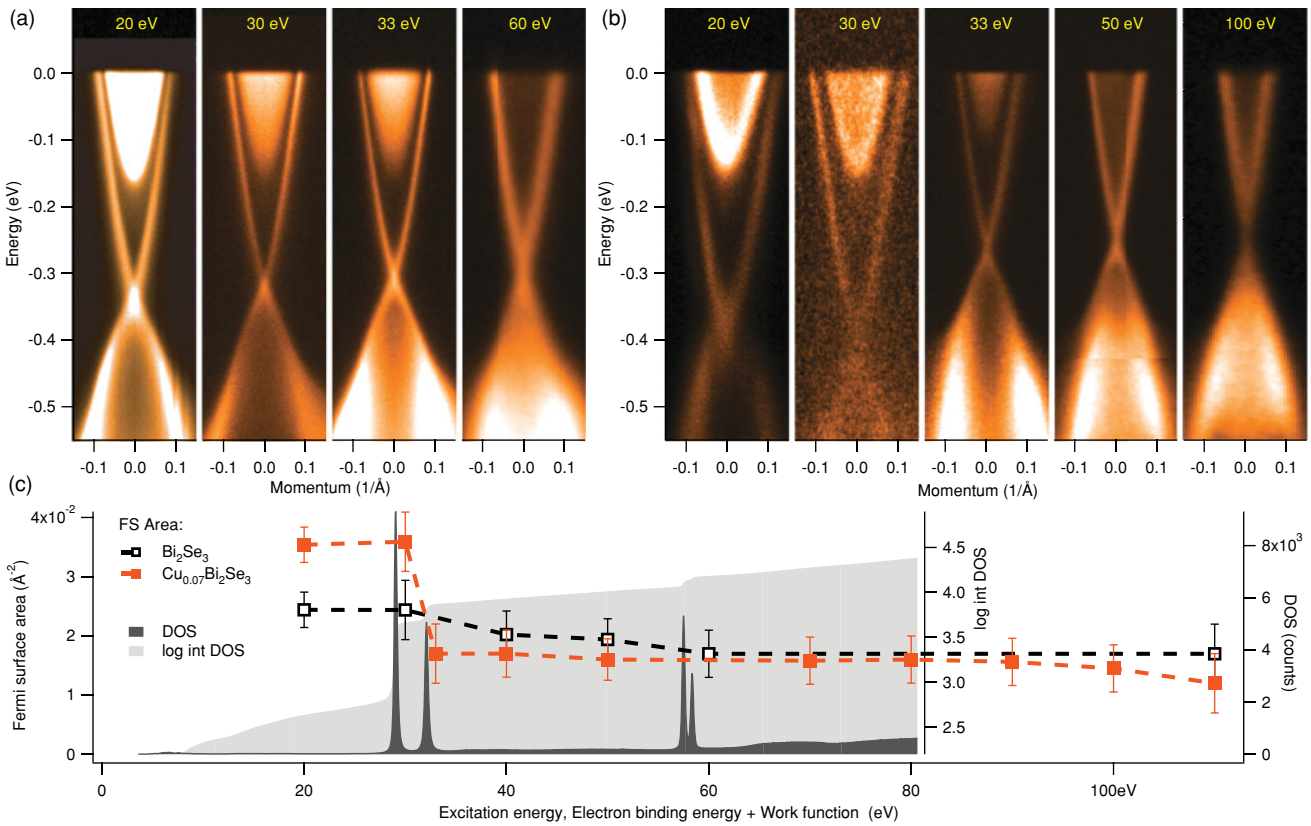

FIG. 2. (Color online) Excitation energy dependence of the surface-state occupancy. A weak decrease of the binding energy of the Dirac point in Bi_2Se_3 (a) is contrasted to a 150 meV steplike change in $Cu_{0.07}Bi_2Se_3$ (b). (c) The step at 30 eV in the surface-state occupancy, shown in units of the Fermi surface area, corresponds to the lowest photon energy enabling photoemission from Bi 5*d* core levels and consequent manifold increase of the photocurrent [see underlying plot of integral density of states (DOS)].

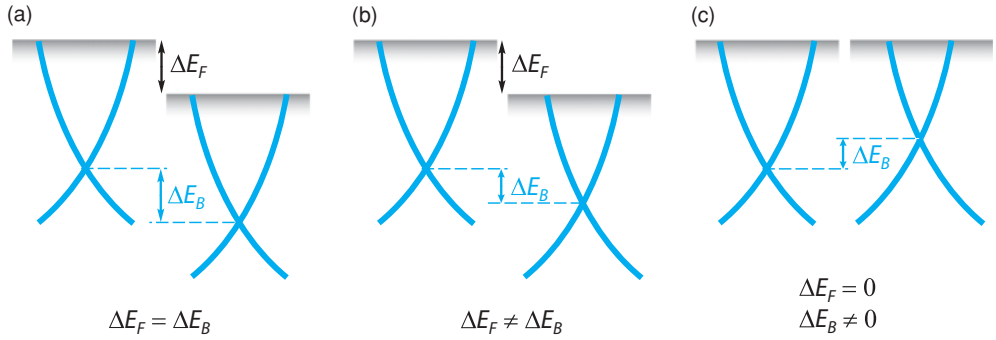

FIG. 3. (Color online) A classification of the photovoltage effects as seen by photoemission. (a) A so-called charging of the whole sample due to absence of a good Ohmic contact between the surface of the sample and the electron analyzer appears as a shift ΔE_F of the Fermi level E_F of the sample under illumination with respect to its equilibrium position or to the E_F of the analyzer. (b) In the most general case the light-induced photovoltage both affects the surface charge region and creates the charge of the sample. (c) In the case of a highly conductive surface (and poorly conductive or insulating sample volume), its Fermi level remains equal to that of the analyzer and the only observed photovoltage effect is the surface-state gating.

function ϕ. Thus, one may expect an abrupt change in electron concentration at those energies. Indeed, the energy around 30 eV at which the Dirac cone occupancy in Cu-intercalated Bi_2Se_3 changes by a factor of 2 corresponds to the lowest binding energy of the core electrons in this compound. The energy levels of those electrons are seen as two narrow peaks around 30 eV and can be unambiguously associated with the Bi $5d_{5/2}$ and $5d_{3/2}$ electrons residing at 23.8 and 26.9 eV binding energies,[17] respectively ($\phi = 4.3$ eV). The integral density of states [shown in Fig. 2(c) as a gray shaded area], which should be roughly proportional to the photocurrent, changes by more than ten times at this absorption step. This allows one to conclude that the observed change in the surface-state occupancy is caused by a photovoltage effect.

The photovoltage effect on semiconducting surfaces and interfaces has been studied since the late 1940s,[18] and the surface photovoltage method has been used as an extensive source of surface and bulk information on various semiconductors and semiconductor interfaces[19,20] but, despite the great body of work, a microscopic description of the effect and related band bending is missing. In this regard, ARPES studies of the topologically protected surface states can provide indispensable information for understanding the macroscopic parameters of the photovoltage effect, starting from the electronic band structure of the surface states. On the other hand, the observed effect is peculiar since we see no detectable shift of the Fermi level of the sample with respect to the Fermi level of the spectrometer, which would be expected for a semiconducting sample with a grounded Ohmic back contact[20] (see Fig. 3). This can happen if some volume of the sample under the light spot is charged because of very low interlayer conductivity while the surface of the crystal remains neutral due to good conductivity of the topmost layer, which may be a consequence of a topological protection of the surface states[3] or formation at the surface of a two-dimensional electron gas.[21]

Naturally, the photoinduced gating will be material dependent and particularly sensitive to the interlayer conductivity. One would expect that when the conductivity is lower the gating effect is higher. Thus, the intercalation, by increasing the interlayer distance, decreases the conductivity and increases the gating effect. This is consistent with both the observed enhancement of the effect in Cu-intercalated Bi_2Se_3 as compared to pure Bi_2Se_3 and the resistivity values measured for these crystals. We note, however, that it is difficult to make a quantitative comparison between ARPES and transport since the transport measurements provide us with bulk information while the effect appears in a very narrow surface region in which the local conductivity should be different due to band bending. Also, it is clear that, due to the number of parameters involved, the microscopic understanding of this effect requires thorough investigation of its dependence on photon flux, temperature, and doping. In this Rapid Communication, we have intended to show the robustness of the gating effect in $Cu_{0.07}Bi_2Se_3$ and its correlation with the photoinduced current. Also we note that the accuracy of the present experiment [see the error bars in Fig. 2(c)] does not allow us to draw conclusions about the size of the effect for pure crystals. In this case, it is important to add that a small photovoltage effect for epitaxial Bi_2Se_3 films has been very recently discussed in Ref. 22.

In summary, we observed the effect of photoemission-induced gating of the topological surface states on $Cu_xBi_2Se_3$ which may stimulate the use of topological insulators in electronics.[8,9] The observed enhancement of the effect by Cu intercalation shows the way to control it from the material side. While the peculiarities caused by the presence of the topologically protected surface states have to be understood, the very fact that the photovoltage effect has been observed directly for a compound in which the surface state dispersion can be measured in detail and controlled opens the opportunity to study the microscopic mechanisms of surface photovoltage effects on semiconducting surfaces and interfaces.

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