Experimental verification of a temperature-induced topological phase transition in $TlBiS_2$ and $TlBiSe_2$

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Temperature dependence of the band structure, as well as the spin-polarization on the topologically trivial insulator $TlBiS_2$ and nontrivial insulator $TlBiSe_2$, have been investigated by spin- and angle-resolved photoelectron spectroscopy. Despite the recent theoretical prediction [Phys. Rev. Lett. **117**, 246401 (2016).], topological phase transition (trivial to nontrivial for $TlBiS_2$, nontrivial to trivial for $TlBiSe_2$) does not occur in the observed temperature ranges (from 50 to 400 K for $TlBiS_2$, from 50 to 475 K for $TlBiSe_2$). Our results indicate that the discrepancy between the theory and the experiment can be understood by considering the overestimation of lattice parameters and the effect of lattice expansion that is neglected in the previous theory. Although some spin-polarized states are observed in $TlBiS_2$, it is probably due to the Rashba-like surface (resonant) states and not the topological surface states. On the other hand, the topological surface states in $TlBiSe_2$ is very robust even at 400 K and the spin-polarized states can be used for the real spintronic devices in the large temperature range.

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I. INTRODUCTION

Topological insulators (TIs) and their related materials are getting tremendous attentions in recent decades because of their potentials for the applications of spintronic devices. For the practical use of them in the real devices, the stability of the electronic states and the spinpolarization is important. On the other hand, a phase transition or control of the electronic states by some perturbation such as electric field [1], temperature [2], pressure [3,4], and so on, might be also useful for the spintronics application.

Tl based ternary chalcogenide $TlBiSe_2$ is one of the most ideal topological insulators, which possesses well separated topological surface states (TSSs) in the bulk bandgap and fast group velocity [5,6]. In addition, by controlling the stoichiometry slightly one can adjust the Dirac point with bulk insulating property at the Fermi level [7,8]. Furthermore, the possibility of topological phase transition (TPT) mediated by electron-phonon coupling has been theoretically predicted by Antonius and coworker in the $TlBiSe_2$ and the related material $TlBiS_2$ [9]. Very recently, Lihm and Park also predicted the phonon-induced TPT in $TlBiSe_2$ [10]. According to the theory, a topologically nontrivial $TlBiSe_2$ changes into topologically trivial phase by increasing temperature at about 240 K (311 K in Ref. [10]). On the other hand, in the case of $TlBiS_2$ the phase transition from topologically trivial to nontrivial phase occurs at about 260 K. Since the phase transition from topologically trivial to nontrivial states by changing the ratio of S and Se in $TlBi(S_xSe_{1-x})_2$ has been reported so far [11,12], the system has the possibility of phase transition. However, the experimental verification of temperature induced TPT in these systems has not yet been reported.

In this report, we have examined the TPT on both $TlBiSe_2$ and $TlBiS_2$ by observing the evolution of electronic structure with changing the temperature from 50 to more than 400 K. Contrary to the theoretical prediction, no phase transition is observed both in $TlBiSe_2$ and $TlBiS_2$. That is, no sign of TSSs is observed in $TlBiS_2$ (topologically trivial in the ground state) by an angle-resolved photoelectron spectroscopy (ARPES) measurement with changing temperature. On the other hand, TSSs of $TlBiSe_2$ (topologically nontrivial in the ground state) are persistent even at the higher temperature than the predicted phase transition temperature.

II. EXPERIMENTAL METHODS

All the experiments were done at the ESPRESSO endstation [13] at the beamline BL-9B of Hiroshima Synchrotron Radiation Center (HiSOR) dedicated to spin- and angle-resolved photoelectron spectroscopy (spin-ARPES). $TlBiS_2$ and $TlBiSe_2$ single crystals were grown by the Bridgman method and cleaved in an ultra-high-vacuum chamber. Since the bulk Γ point of these materials can be approached at $h\nu \sim 18$ eV in normal emission condition [6], p–polarized

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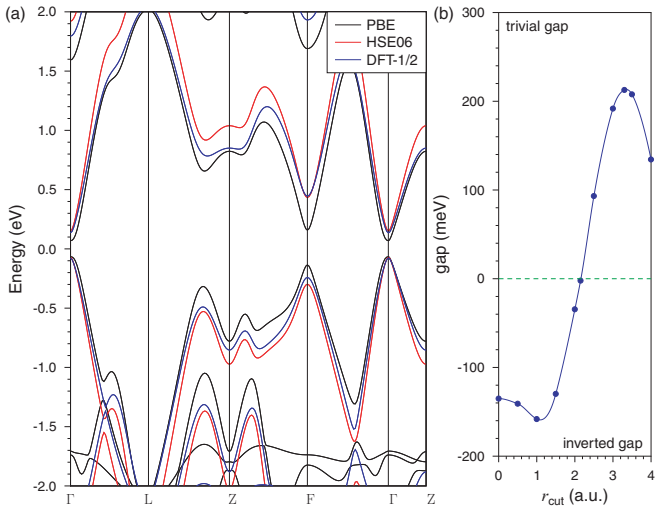

FIG. 1. (a) Bulk band structure of $TlBiS_2$ calculated within PBE, HSE06, and DFT-1/2 approaches. (b) Dependence of the Γ gap on the r_{cut} for the atomic self-energy potential V_S of sulfur. Negative and positive values of the gap correspond to topological nontrivial and trivial phases, respectively.

light at the photon energy from APPLE II type undulator was applied for the (spin-)ARPES measurement.

The temperature dependence of the electronic band structures of $TlBiS_2$ ($TlBiSe_2$) were measured at the temperature range of 50 K $\sim$ 400 K (475 K) by using the 6-axes goniometer equipped with He cryostat and electric heater. The base pressure of the analysis chamber was 5×10^{-9} Pa and the pressure was kept lower than 2×10^{-7} Pa during the measurement at the high temperature.

III. COMPUTATIONAL METHOD AND BULK BAND STRUCTURE

The density functional theory (DFT) calculations were performed by using the Vienna *ab initio* Simulation Package (VASP) [14,15], with core electrons represented by projector augmented wave potentials [16,17]. Since DFT calculations for $TlBiSe_2$ were earlier presented elsewhere [18–20] we focus here on $TlBiS_2$ only. The generalized gradient approximation of Perdew-Burke-Ernzerhof functional (GGA-PBE) [21] for the exchange-correlation potential and DFT-D3 van der Waals correction [22] were applied for structure optimization. Spin-orbit interaction (SOI) was included in all types of calculations. The calculated structural parameters of $TlBiS_2$: $a = 4.1035$, $c = 21.7239$ Å and $z_S = \pm 0.2394$ are in very good agreement with experimental data ($a = 4.1041$, $c = 21.872$ Å and $z_S = \pm 0.2624$) [23]. At equilibrium lattice parameters GGA-PBE gives the gap of 135 meV at the Γ point [Fig. 1(a)], however, according to $\mathbb{Z}_2$ topological invariant calculation, this gap is nontrivial contradicting the experiment. To obtain accurate bulk band structure the HSE06 screened hybrid functional [24] was adopted. The HSE06 derived gap equals to 221 meV and it is characterized by trivial $\mathbb{Z}_2$ invariant. Note that for $TlBiSe_2$ both GGA-PBE and HSE06 calculations predict a nontrivial topological phase, although the bandgap differs significantly.

For surface band structure calculations we used a slab model and apply the DFT-1/2 self-energy correction method [25,26]. This method yields accurate band structures for many semiconductors and owing to its low computational cost, DFT-1/2 can be considered as a good alternative to very expensive hybrid functional methods for systems that require large computational cells. The DFT-1/2 approach only requires the addition of a self-energy correction potential, calculated from a partially ionized free (anion) atom, to the standard DFT potential [26]. The cut-off radius r_{cut} in spherical step function multiplier for atomic self-energy potential V_S is the only parameter of the method [25,26], which is determined variationally by maximizing the bandgap. As can be seen in Fig. 1 (b), variation of r_{cut} allows receiving non-inverted (trivial) gap of 213 meV in fine agreement with the HSE06 results. To mimic the nonpolar conditions of the cleavage surface unveiled by scanning tunneling microscopy [27] we utilized the slab of 33 atomic layer thickness with the simplest reconstruction $\sqrt{3} \times 1$ with one Tl surface atom removed [see Fig. 4(a)], and hence such a reconstruction contains anion and cation atoms on the surface.

IV. RESULTS AND DISCUSSION

A. $TlBiS_2$

Figure 2(a) shows experimental electronic band dispersion of $TlBiS_2$ along the $\bar{\Gamma} - \bar{M}$ direction taken at different sample temperatures. At the $\bar{\Gamma}$ point, at 100 K, one can clearly see parabolic bands with downward and upward dispersions that are separated with the energy gap. A natural electron doping caused by inevitable bulk vacancies let both bulk conduction and valence bands come into sight at this temperature. At the higher binding energies, a small M-shaped band (dotted line) and a large M-shaped band (dashed line) are also observed. The observed bands at 100 K are in good agreement with the previously reported ARPES results on $TlBiS_2$ [11,12] and is consistent with the topologically trivial electronic structure at the ground state. As seen in the figure, by increasing temperature, all the bands shift to lower binding energies and the conduction band shifts above the Fermi level at T > 350 K. The possible reason for the band shifts is due to the change of surface band bending associated with the change of the surface condition. However, no obvious change of the band structure is observed.

In order to see more precisely the evolution of the band structure near the energy bandgap, the zoomed images with modified contrasts of the band dispersion near the bulk bandgap are shown in Fig. 2(b). As in the figure (and Fig. 1S in Supplemental Material [28]), no indication of TSSs' appearance in the bulk bandgap above the predicted transition temperature (260 K) and no clear evidence of TPT are observed even at the highest temperature (400 K) of our experiment.

Although the TSSs do not appear in the measurement temperature range, there might be a possibility that the TPT temperature is much higher than the theoretical prediction. To examine the possibility, the temperature dependence of the energy gap between conduction and valence bands is plotted in Fig. 3. Here, the bulk band-gap size is estimated from the

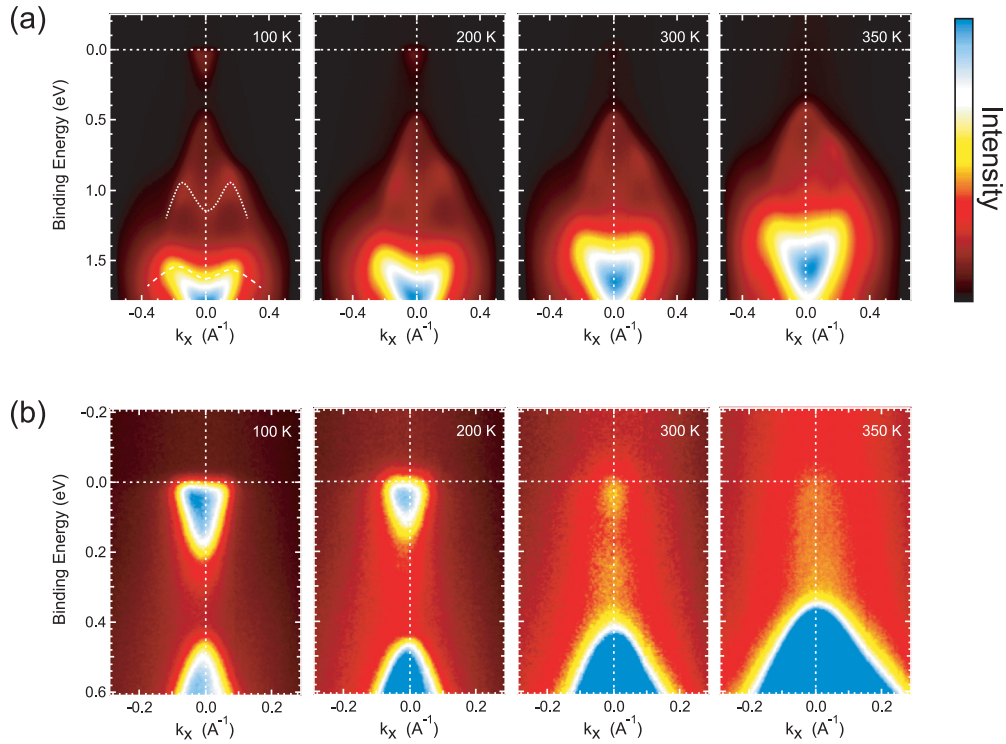

FIG. 2. (a) Temperature dependence of the band structure of $TlBiS_2$ along the $\bar{\Gamma} - \bar{M}$ direction.(b) Enlarged and contrast enhanced images at the bulk band-gap region in (a).

offsets of the conduction and valence band spectra at the $\bar{\Gamma}$ point.

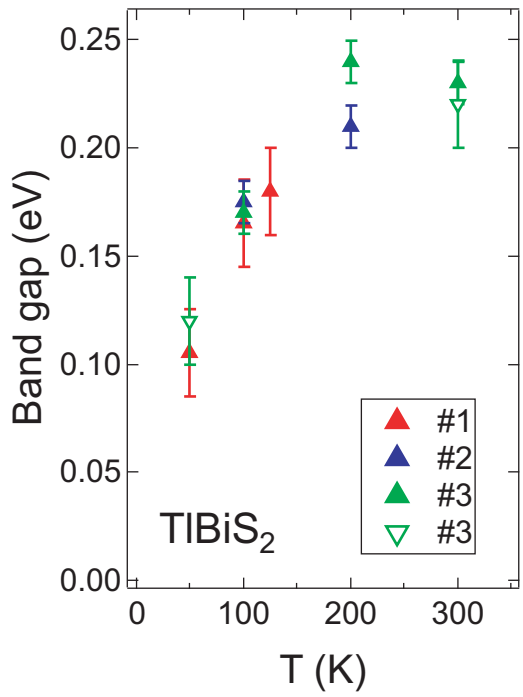

FIG. 3. (a) Temperature dependence of the bulk bandgap of $TlBiS_2$. The different colors (and # number) mean different samples and the upward (downward) triangles indicate the measurement in heating (cooling) process.

Since the conduction band shifts above the Fermi level at 350 K, we plotted the values up to 300 K. As in the figure, with increasing sample temperature, the bulk bandgap increases from about 0.12 to about 0.23 eV. We have measured the temperature dependence with increasing and decreasing temperature several times, and the tendency of the bulk band-gap increase with temperature rise is reproducible. The observed change of bulk band-gap size is opposite to the theoretical prediction where the bulk bandgap is predicted to reduce toward the bulk band inversion which is the prerequisite to induce the TPT. Therefore, the topological phase transition will not occur in $TlBiS_2$ even at the higher temperature.

One of the possible reasons for the discrepancy between the theoretical prediction and the experiment is the effect of lattice expansion which is neglected in the previous calculation by Antonius and coworkers [9]. In the case of trivial state of $TlBiS_2$, the conduction and valence bands of the system mainly consist of bonding state of Bi p_z orbital and the anti-bonding state of S p_z orbital, respectively. In the simple consideration, it is expected that the expansion of the lattice causes the reduction of band widths and the upward shift of bonding state of Bi p_z band and the downward shift of antibonding state of S p_z band. Thus, the energy gap between the bonding state of Bi p_z and antibonding state of S p_z will increase by the lattice expansion, which is the opposite behavior to the band inversion between the bonding and antibonding state that is necessary for the TPT.

Furthermore, according to our first-principles calculation, the energy gap is sensitive to the size of the lattice (or volume) and especially to the c/a ratio, which mainly determines the distance between Bi and S layers and hence the

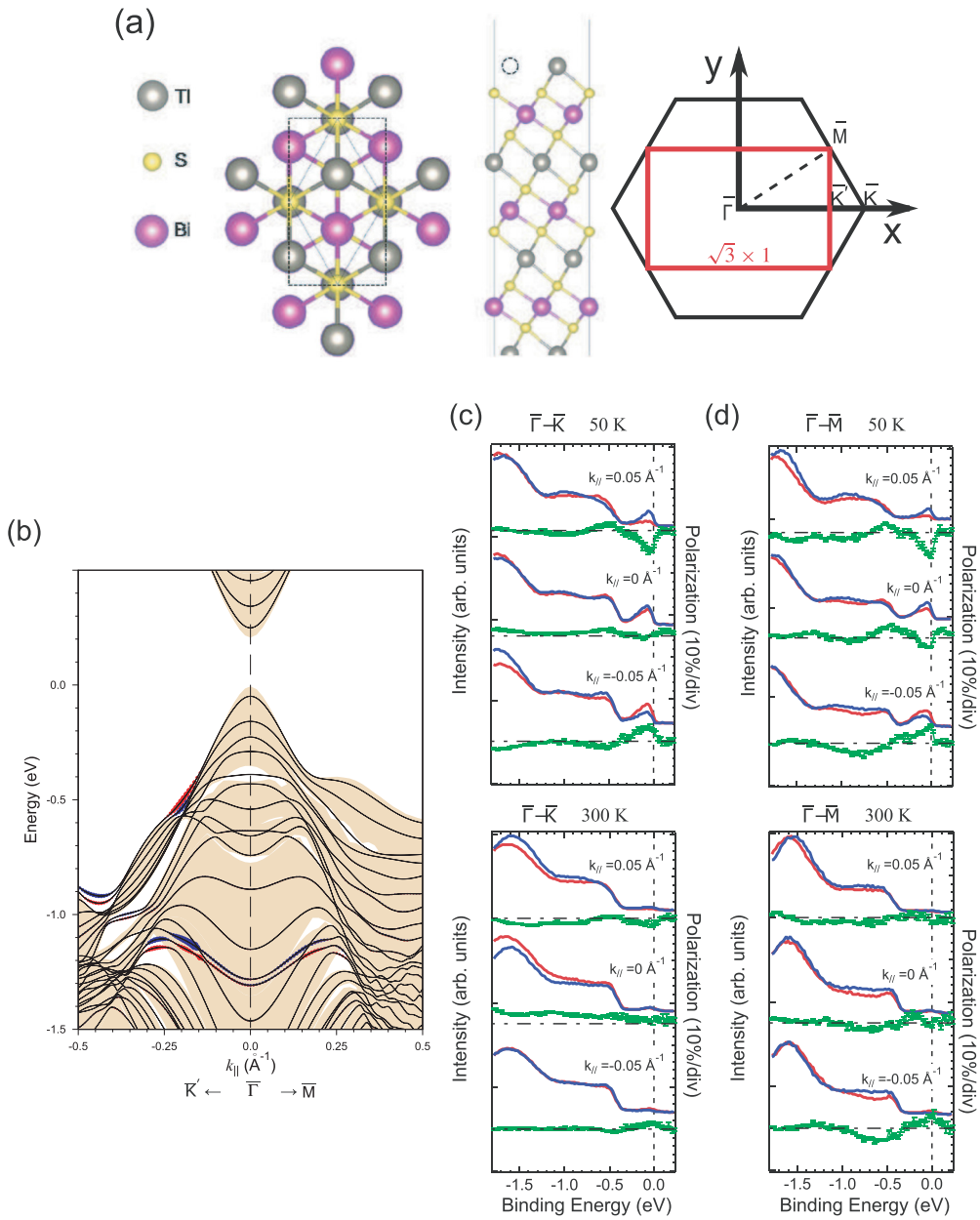

FIG. 4. (a) Atomic structure (top view: left, side view: in the middle) of the $TlBiS_2$ $\sqrt{3} \times 1$ slab used for the surface band structure calculation and corresponding surface Brillouin zone (right). The dashed circle in the middle panel shows the missing Tl surface atom. (b) Calculated surface electronic structure. (c) Spin up (red) and spin down (blue) photoemission spectra as well as the spin polarization (green) of $TlBiS_2$ taken by spin-ARPES measurement at lower temperature (50 K) and higher temperature (300 K) along the $\bar{\Gamma} - \bar{K}$ direction at $k_{\parallel} = -0.05$, 0, and 0.05 Å^{-1}. (d) The same as (c) but along the $\bar{\Gamma} - \bar{M}$ direction.

hybridization of their p_z orbitals. Although the bandgap obtained in HSE06 calculation is about 220 meV and larger than the experiment, only 0.3% volume reduction causes the band-gap reduction of about 100 meV, which is consistent with the gap change behavior observed in our experiments. Considering the dependence of the gap on c/a ratio we found that starting from $c/a = 5.294$ in the equilibrium structure with the HSE06 gap of 221 meV the decrease in c/a leads to a rapid linear reduction in the gap width and at $c/a = 5.017$ it becomes zero, after which, with further decrease in c/a the gap turns to the topological phase. At that, the change in lattice volume in the TPT point is relatively small, $V/V_0 = 0.994$. Thus, our results imply that it is important to take the temperature induced lattice expansion into account for the prediction of TPT. The importance of including thermal expansion for the investigation of TPT has also been shown by the previous theoretical study on the family of Bi_2Se_3 [4].

According to the previous DFT calculations by Singh and coworkers [3], it is expected that the compression of the $TlBiS_2$ system along the c axis causes the band inversion and the topological phase transition, being consistent with the tendency of our experimental results. However, it should be noted that a large lattice reduction (about 5%) is expected for the phase transition in their calculation and also the

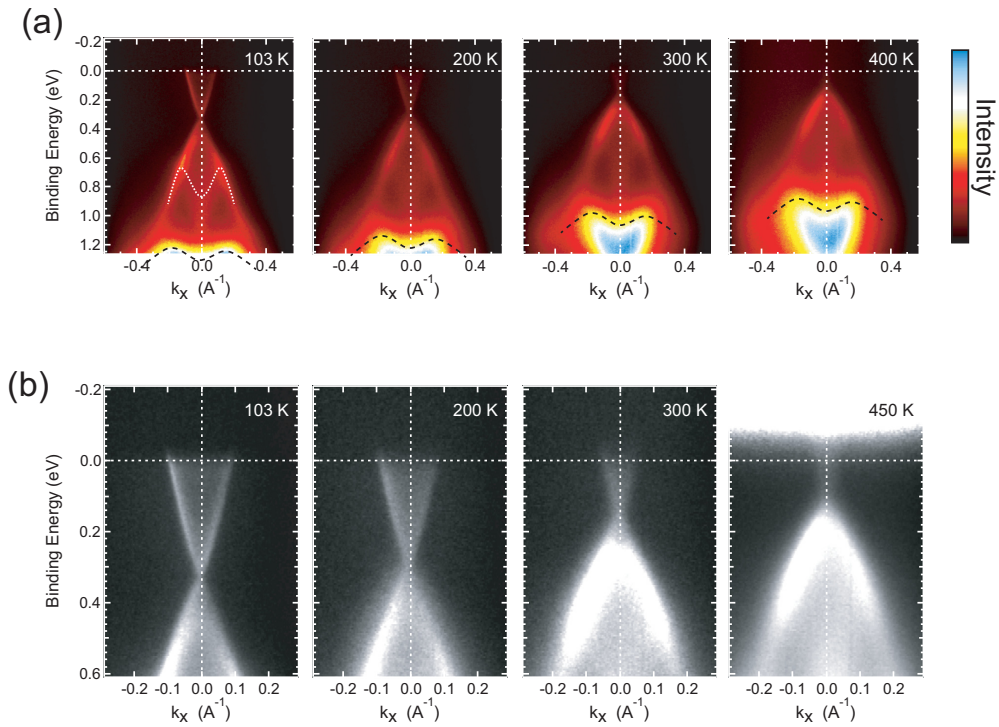

FIG. 5. (a) Temperature dependence of the band structure of $TlBiSe_2$ along $\bar{\Gamma} - \bar{K}$. (b) Enlarged and intensity enhanced images around the Dirac point in (a). The image of 450 K is divided by the Fermi distribution function in order to enhance the states above the Fermi level.

equilibrium lattice parameters in Ref. [3] correspond to the unit cell volume by 4.2% expanded as compared to the experimental data [23]. At the same time, the cell volume calculated in Ref. [9] exceeds the experimental volume even more, by 8%. Thus, this result confirms that, as we have shown above, the standard DFT gives an incorrect topological phase for $TlBiS_2$ at experimental (or close to them) lattice parameters. Since the temperature-induced lattice expansions are usually relatively small (less than a percent), the initial error of the starting lattice parameters in the paper of Antonius *et al.* [9] is an order of magnitude greater than the possible temperature effect and might be a main reason for the discrepancy between the theory and our experimental results.

Although no sign of TSSs has been observed in the ARPES measurement we have investigated the spin polarization of the electronic structure of $TlBiS_2$ by spin-ARPES measurement. Figures 4(c) and 4(d) show the spin-ARPES spectra of $TlBiS_2$ at $k_{\parallel} = -0.05, 0, 0.05$ Å^{-1} along $\bar{\Gamma} - \bar{K}$ and $\bar{\Gamma} - \bar{M}$, respectively, at a temperature below (50 K) and above (300 K), the proposed transition temperature (260 K). Contrary to the previous report [29], in both directions considerable spin polarization is observed both at below and above the proposed transition temperature. Although the origin of the spin polarization is not evident and a possibility of photoemission final state effect cannot be excluded, the sign reversal with respect to the $\bar{\Gamma}$ point implies that the spin polarization is likely to be due to the Rashba effect and principally being consistent with our calculation as will be discussed below. The unchanged spin texture between below and above the topological phase transition temperature predicted by Antonius *et al.* [9], however, implies that the observed spin texture is not because of the emergence of TSSs. The reduction of the degree of spin polarization at higher temperature also implies that the origin of spin-polarized states is not TPT.

The calculated surface electronic states of nonpolar $\sqrt{3} \times 1$ $TlBiS_2$ surface [Fig. 4(a)] is shown in Fig. 4(b). The $\bar{\Gamma} - \bar{K}'$ direction in the $\sqrt{3} \times 1$ surface Brillouin zone (SBZ) coincides with the $\bar{\Gamma} - \bar{K}$ direction of original 1×1 SBZ and the $\bar{\Gamma} - \bar{M}$ directions completely match in both SBZs [Fig. 4(a)]. The calculated band structure reproduces very well in the experimentally observed up- and down-convex parabolic bands at the $\bar{\Gamma}$ point. The results of the first-principles calculation indicate that some surface states possess Rashba-like spin polarization in the $\bar{\Gamma} - \bar{K}'$ direction (they are observed at larger $k_{\parallel}$ than in the experiment). However, the calculations do not reveal the spin-split surface states in the $\bar{\Gamma} - \bar{M}$ direction. The small discrepancy with the experiment can be attributed to simplification of the surface structure in our simulation compared to the real complex structure of the surface in the $TlBiX_2$ compounds [27]. Thus, the origin of observed spin polarization in our spin-ARPES measurement is probably due to these Rashba-like surface states and not because of the TSSs.

B. $TlBiSe_2$

In contrast to the $TlBiS_2$, $TlBiSe_2$ is topologically nontrivial in the ground state. As in Fig. 5, clear linear dispersion of Dirac cone is observed at 103 K, which is taken at $h\nu$=18 eV along the $\bar{\Gamma} - \bar{K}$ direction. Because of the natural doping by the defects [27] the Dirac point (DP) is shifted to higher binding energy and located at about $E_B = 0.33$ eV at 103 K. In addition to the Dirac cone, some bulk bands [small and large M-shaped bands (dotted and dashed lines)], which are

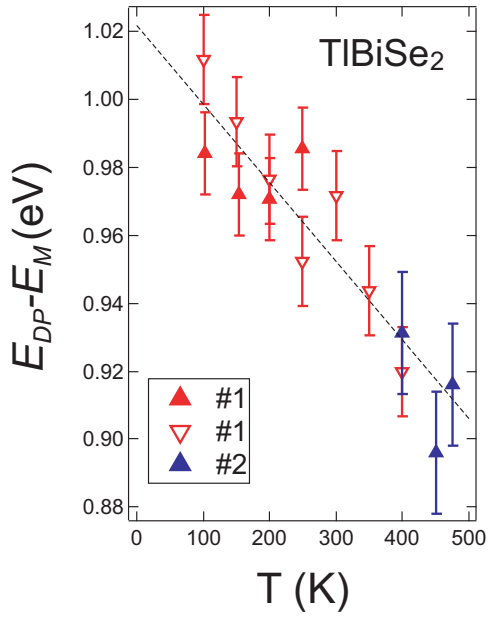

FIG. 6. Temperature dependence of the energy difference between DP and the top of the large M band of $TlBiSe_2$. Different colors (and # numbers) mean different samples and the upward (downward) triangles indicate the measurement in heating (cooling) process. The dashed line is the result of the line fit of the data points.

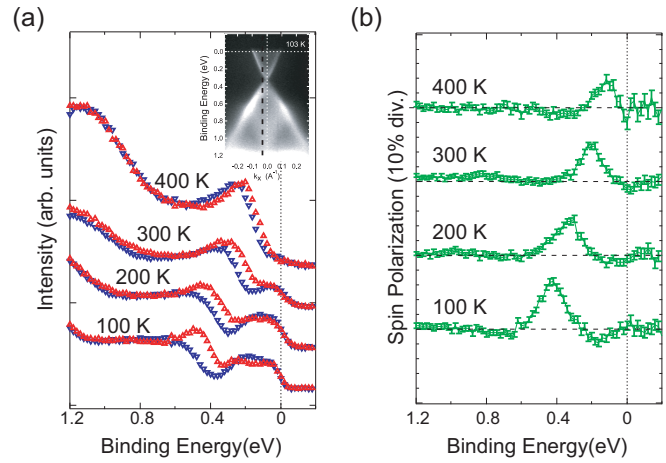

FIG. 7. (a) Temperature dependence of the spin-resolved ARPES spectra at $k = -0.03$Å^{-1} along the $\bar{\Gamma} - \bar{\mathrm{K}}$ direction of $TlBiSe_2$ and (b) the corresponding spin-polarization spectra. The dashed line in the inset is the position of the spin-ARPES measurement. Upward (downward) triangles in (a) represent spin up (down) states.

similar to the $TlBiS_2$ sample are observed at higher binding energies than the DP. The bulk conduction band is, however, hardly seen probably because of the matrix element effect at this photon energy. Similar to the $TlBiS_2$ system, these bands shift almost rigidly to the lower binding energies with increasing temperature. As seen clearly in Fig. 5(b), which shows expanded images near the DP of Fig. 5(a), even at higher temperatures than the theoretically predicted TPT temperature (∼240 K[9]), the TSSs still remain and neither disappearance of the TSS nor gap opening at DP is observed at 300 K. Though the bands blur a bit, the gapless TSSs are still observed at 450 K. Therefore, in the measured temperature range, no evidence of the TPT has been observed.

In order to examine the possibility of the phase transition at much higher temperature, we have investigated the change of the bandgap as the function of temperature. Since the bulk conduction band (the band above DP) is not well observed in our experiment, we plotted the energy difference between the top of the large M-shaped bulk band (dashed line) and the DP ($E_{DP} - E_M$) in Fig. 6. Although the energy difference does not indicate the bulk band gap directly, it probably shows the tendency of the temperature dependence of the bulk bandgap. In contrast to the $TlBiS_2$ case, reduction of the energy difference (i.e., bulk energy gap) with increasing temperature is observed both in the measurement with heating and cooling the sample. This reduction of the energy difference is along the line of theoretical prediction. The reduction rate is estimated as $2.3 \times 10^{-4} \pm 3 \times 10^{-5}$ eV/K from the line fit of the data as indicated with the dashed line in Fig. 6. Considering the original bandgap of $TlBiSe_2$ that is reported as 0.35 eV at the $\bar{\Gamma}$ point [12], and assuming that the estimated energy reduction is half of the reduction of the bandgap, the critical temperature of the phase transition can be roughly estimated as around 760 K, which is quite higher than the room temperature.

The discrepancy between the experiment and the previous theory is likely to be ascribed to the overestimation of lattice parameters in the calculation presented in Ref. [9], in which about 9.8% larger volume (3.14% larger a and 3.26% larger c) than the experimentally observed ones [30] is used. This overestimation probably induces the smaller bandgap (∼0.1 eV) in the ground state in the calculation than the real bandgap (∼0.35 eV). The smaller bandgap results in the lower transition temperature in the calculation. The lattice parameters used in Ref. [10] were not reported, however the gap at $T = 0$ estimated as ≈132 meV is also too small comparing with experimental value. Additionally, the effect of thermal expansion was neglected in this work that predicted electron-phonon-assisted topological phase transition at 311 K.

As in the case of $TlBiS_2$, the lattice expansion by heating must affect to the temperature dependence of the electronic structure. As discussed above, in the case of the topologically nontrivial $TlBiSe_2$, the lattice expansion can work to reduce the inverted bulk band and it is in line with the occurrence of topological phase transition. However, the expansion should be much smaller than 9.8% and is too small to promote the phase transition.

We have also measured the spin polarization of the Dirac cone below and above the proposed transition temperature. In Fig. 7 we show the temperature dependence of (a) spin-resolved ARPES spectra at $k_{\parallel} = -0.03$ Å^{-1} and (b) the corresponding spin polarization. Although the DP shifts to lower binding energies with increasing temperature because of the rigid band shift, quite high spin-polarization is observed and the spin-polarization of lower Dirac cone is more than 20% even at 400 K. The robustness of the TSSs of $TlBiSe_2$ at the high temperature must be useful in the realization of spintronic devices.

V. CONCLUSION

The evolution of electronic structures of $TlBiS_2$ and $TlBiSe_2$ has been experimentally investigated with changing temperature (50–400 K in $TlBiS_2$ and 50–475 K in $TlBiSe_2$). In contrast to the previous theoretical prediction, no clear evidence of TPT such as the emergence (disappearance) of TSS is observed in $TlBiS_2$($TlBiSe_2$). The observed temperature dependence of the bulk band energy gap in $TlBiS_2$ is opposite to the previous theoretical prediction and the TPT will not occur even at much higher temperature. The discrepancy between the previous DFT results and the experiment is mainly due to the overestimation of the lattice parameters as well as the neglect of effect of lattice expansion, which enhances the energy gap of trivial bandgap in the previous theory.

In the $TlBiSe_2$, the temperature dependence of the bulk bandgap is in line with the theoretical prediction. However, the experimentally observed large bulk bandgap in the $TlBiSe_2$ (0.35 eV) will be hardly closed until a quite high temperature ($\sim$ 760 K). The small bulk bandgap obtained by the previous calculation using about 10% larger bulk cell volume than the experimentally obtained one leads the lower phase transition temperature than reality. On the other hand, observed persistency of the spin-polarized states of $TlBiSe_2$ at higher temperature than room temperature will be a good property for the realization of spintronic devices in the future.

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