

## Reply to “Comment on ‘Instability of the topological surface state in Bi<sub>2</sub>Se<sub>3</sub> upon deposition of gold’”

A. Polyakov,<sup>1</sup> C. Tusche,<sup>2,1</sup> M. Ellguth,<sup>3,1</sup> E. D. Crozier,<sup>4</sup> K. Mohseni,<sup>1</sup> M. M. Otrokov,<sup>5,6,7</sup> X. Zubizarreta,<sup>1</sup> M. G. Vergniory,<sup>1,8</sup> M. Geilhufe,<sup>1,9</sup> E. V. Chulkov,<sup>8,6,5</sup> A. Ernst,<sup>1,10,\*</sup> H. L. Meyerheim,<sup>1,†</sup> and S. S. P. Parkin<sup>1</sup>

<sup>1</sup>Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany

<sup>2</sup>Peter Grünberg Institut (PGI-6), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

<sup>3</sup>Johannes-Gutenberg-Universität Mainz, Institut für Physik, Staudingerweg 7, 55116 Mainz, Germany

<sup>4</sup>Department of Physics, Simon Fraser University, Burnaby, BC Canada, V5A 1S6

<sup>5</sup>Departamento de Física de Materiales UPV/EHU, Centro de Física de Materiales CFM - MPC and Centro Mixto CSIC-UPV/EHU, 20080 San Sebastián/Donostia, Basque Country, Spain

<sup>6</sup>Tomsk State University, 634050 Tomsk, Russia

<sup>7</sup>Saint Petersburg State University, 198505 Saint Petersburg, Russia

<sup>8</sup>Donostia International Physics Center (DIPC), 20018 San Sebastián/Donostia, Basque Country, Spain

<sup>9</sup>Nordita, Stockholm Center for Quantum Materials, KTH Royal Institute of Technology and Stockholm University, Roslagstullsbacken 23, SE-106 91 Stockholm, Sweden

<sup>10</sup>Institute for Theoretical Physics, Johannes Kepler University, A-4040 Linz, Austria



(Received 24 February 2018; published 31 October 2018)

In the Comment on our publication [Phys. Rev. B **95**, 180202(R) (2017)], R. A. Gordon claims that our main conclusion is not valid, namely that gold atoms deposited *in situ* on the (0001) surface of single-crystalline Bi<sub>2</sub>Se<sub>3</sub> reside in substitutional sites, i.e., replacing bismuth atoms within the topmost quintuple layer (QL). Based on x-ray absorption near-edge (XANES) spectra and a re-evaluation of extended x-ray absorption fine structure (EXAFS) data above the Au *L*<sub>III</sub> edge, R. A. Gordon concludes that Au resides in a twofold environment as a result of an interface reaction leading to an Au<sub>2</sub>S-type local structure, in which gold adopts an Au(I) state and is linearly coordinated by selenium atoms. In this Reply, we will confirm the results published in the original paper and their interpretation that Au atoms reside in the substitutional site.

DOI: [10.1103/PhysRevB.98.136202](https://doi.org/10.1103/PhysRevB.98.136202)

One of the main conclusions of our study “Instability of the topological surface state in Bi<sub>2</sub>Se<sub>3</sub> upon deposition of gold” by Ref. [1] is that gold atoms deposited *in situ* on the (0001) surface of single crystalline Bi<sub>2</sub>Se<sub>3</sub> reside in substitutional sites, i.e., replacing bismuth atoms within the topmost quintuple layer (QL).

In the Comment on our publication, an alternative model is proposed, which suggests that Au resides in a twofold environment as a result of an interface reaction leading to a Au<sub>2</sub>S bulklike local structure. Here, gold is suggested to adopt an Au(I) state and is twofold and linearly coordinated by a single shell of selenium atoms [2]. This model is worth to be discussed, however, we believe that the substitutional model published in Ref. [1] fits the observed data significantly better. In the following, we discuss the most important arguments that lead us to this conclusion.

In general, under the given experimental conditions (ultra-high vacuum and sample temperature  $T = 170$  K) ultrathin films grown by molecular beam epitaxy are far from thermodynamic equilibrium. Therefore the formation of thermodynamically stable phases such as Au<sub>2</sub>S—even on a local

length scale—cannot be expected *a priori*. Rather, metastable structures may form. In the present case, such a metastable structure is formed by the substitution of the Bi atom by metal atoms. This “substitutional site” has frequently been observed even in cases where the radius  $r$  of the replacing cation (e.g., Cr, Fe, Mn, Cu) is considerably smaller (e.g., Cr<sup>3+</sup>:  $r = 0.76$  Å, Cu<sup>3+</sup>:  $r = 0.68$  Å) than that of the substituted Bi<sup>3+</sup> ( $r = 1.17$  Å) and even smaller than that of the Au<sup>1+</sup> ( $r = 1.29$  Å) or Au<sup>3+</sup> ( $r = 0.99$  Å) cation [3–7]. The radii are given for sixfold coordination [8,9].

In the Comment, it is argued—based on a qualitative comparison of x-ray absorption near-edge spectroscopy (XANES) between spectra collected for the Au/Bi<sub>2</sub>Se<sub>3</sub> film, and bulk Au<sub>2</sub>S and AuCl<sub>3</sub>—that gold is present as Au(I), rather than as Au(III), which is assumed to be the formal charge state when substituting Bi in Bi<sub>2</sub>Se<sub>3</sub>.

XANES probes the density of unoccupied states (DOS) at the Fermi level [ $\rho(E_F)$ ], which is given by the relation  $\mu(E) \propto |M_{fi}|^2 \times \rho(E_F)$ , in which  $M_{fi}$  represents the transition matrix element. The conclusion, which can be drawn from the spectra shown in the Comment, is that both Au<sub>2</sub>S and Au/Bi<sub>2</sub>Se<sub>3</sub> exhibit a *smaller* “pre-edge” feature than the reference AuCl<sub>3</sub>, thus  $\rho(E_F)$  for the AuCl<sub>3</sub> phase is larger than for the two other phases. We think that this is not a proof that Au is *not* in the Bi substitutional site. We argue that in the

\*theory: aernst@mpi-halle.de

†experiment: hmeyerhm@mpi-halle.de

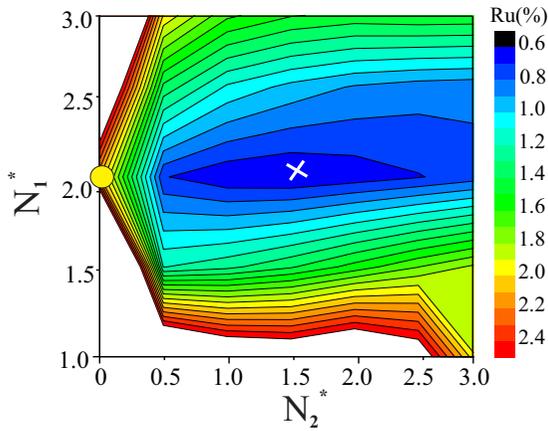


FIG. 1. Contour plot of the residuum (Ru) vs effective coordination number  $N_1^*$  and  $N_2^*$ . The solid point marks the Ru for the single shell fit, the white cross the minimum for the two shell fit. White areas indicate values outside the interval covered by the color code.

metastable substitutional site, the unoccupied DOS at  $E_F$  is not necessarily similar to that in a bulklike structure, which is used as reference, i.e., in this case the “fingerprint technique” may not work. This is especially important here, because as a reference for the  $\text{Au}^{3+}$  state, the bulk compound  $\text{AuCl}_3$  is used, in which Au is bonded to highly electronegative Cl atoms, which strongly attract electrons from the Au atom. By contrast, the electronegativity of both Se and S is considerably lower ( $\approx 2.5$  for Se versus 3.2 for Cl). It is questionable to use the “fingerprint technique” in the case here, where the compounds that are compared are so different in their ability to attract electrons, which may significantly influence the charge density distribution and the empty DOS. Finally, it is not clear whether gold in the substitutional site necessarily adopts the Au(III) state. For instance, multivalent Cr and Mn are also known to substitute  $\text{Bi}^{3+}$  [3–5,7], but so far no consensus regarding the charge state (2+ or 3+) has been found (see e.g., Refs. [6,7,10]).

One of the main arguments in the Comment is that the single shell fit gives a better agreement with the data in terms of the unweighted residuum (Ru) than the one obtained for the two-shell fit derived for the substitutional model (Ru = 1.5% versus 2.3% and 4.3% in Ref. [1] for  $E_{\parallel}$  and  $E_{\perp}$ , respectively). The Ru value for our substitutional model is worse, because in these fits we have fixed the effective coordination numbers  $N_1^*$  and  $N_2^*$  for the first and second shell to the calculated values assuming complete coordination of selenium atoms around the gold atom in the substitutional site. Allowing these to vary drastically improves the fit to values in the 0.7% range, which is at least a *factor of two* better than that obtained for the single shell fit. This is shown in Fig. 1. For direct comparison, we have used the same integration limits for the Fourier transformation (FT) and the same parameters for the peak filtering in  $R$  space as quoted in the Comment. First of all, using the single shell model, we can fairly well reproduce the corresponding fit results with regard to distance  $R$ , the effective coordination number  $N_1^*$ , the mean squared relative displacement  $\sigma^2$ , and the energy

shift  $\Delta E_0$  quoted in the Comment. In Fig. 1, the solid point represents the Ru ( $\approx 2.0$ ) obtained for this model, i.e., for  $N_2^* = 0$ . However, we find that allowing for a second shell, i.e.,  $N_2^* \neq 0$ , drastically improves the fit, which drops to Ru  $\approx 0.70$ .

The minimum is located near  $N_2^* \approx 1.5$  as indicated by the white cross, but a similar fit quality can also be achieved with  $N_2^* \approx 2.5$ – $3.0$ , i.e., it adds to a total effective coordination in the range of  $N_{\text{tot}}^* = 3.5$  to 5.0. In agreement with Ref. [1], distances were found to be  $R_1 = 2.44 \text{ \AA}$  and  $R_2 = 2.65 \text{ \AA}$  with an error bar of  $\Delta R_1 = 0.03 \text{ \AA}$  and  $\Delta R_2 = 0.10 \text{ \AA}$ . Also, the energy shifts  $\Delta E_0$  are below 1 eV, while the magnitudes for  $\sigma^2$  are 0.002 and  $0.015 \text{ \AA}^2$  for the first and second shells, respectively.

At this point, it appears as important to emphasize that the dramatically improved fit quality for the two-shell model relative to the one-shell model also holds if the goodness of fit (GOF), i.e., the normalized  $\chi^2$  parameter, is taken as a measure for the fit quality. It is given by  $\text{GOF} = \sqrt{1/(N - P) \sum [(I_{\text{obs}} - I_{\text{calc}})^2 / \sigma^2]}$  [11], where the difference between observed and calculated intensities is normalized to the uncertainties expressed by the standard deviation  $\sigma$  and  $(N - P)$ , i.e., the difference between the number of data points  $N$  and the number of parameters  $P$ , which are varied. We obtain GOF = 2.52 and 7.06 for the two- and one-shell fit, respectively. Thus the fact that the two-shell fit uses more parameters does not play any role, too large is the improvement of the fit by using two shells.

The interpretation of the two-shell model is that gold atoms reside in the substitutional site, while the selenium atoms relax inward to accommodate the smaller cation [10]. The presence of two nearby selenium shells around a substitutional gold atom comes not unexpected: we recall that in the bulk  $\text{Bi}_2\text{Se}_3$  structure, bismuth atoms in the second and fourth layer of each QL reside in an asymmetric environment with three selenium atoms (first and fifth layer) being closer ( $R = 2.87 \text{ \AA}$ ) than the three selenium atoms in the third layer ( $R = 3.07 \text{ \AA}$ ). Thus one may expect that this asymmetry is also experienced by the gold atoms in this site, even after some structural relaxation.

Furthermore, our model with Au in a highly symmetric environment such as the quasi-octahedral substitutional site naturally explains the polarization *independence* of the EXAFS and NEXAFS amplitude as observed, while for the linear Se-Au-Se environment proposed in the Comment a very strong polarization dependence of the EXAFS and NEXAFS amplitude would be observed:  $N^* = 1.4$  for  $E_{\perp}$  and  $N^* = 3.2$  for  $E_{\parallel}$ , i.e., the difference is more than 100%. The only way to explain the discrepancy is to assume a spatial averaging of the Se-Au-Se chain orientation. The model must assume that the Se-Au-Se chains are arranged vertically and parallel to the surface plane with the same probability. Another possibility is a completely random orientation. But, in view of the intrinsic high anisotropy of the  $\text{Bi}_2\text{Se}_3$  structure composed of alternating Se-Bi-Se-Bi-Se layers only *parallel* to the surface, such a formation of differently oriented domains *with the same volume fraction* appears as very unlikely, especially when one recalls that the gold deposition was carried out at 170 K substrate temperature.

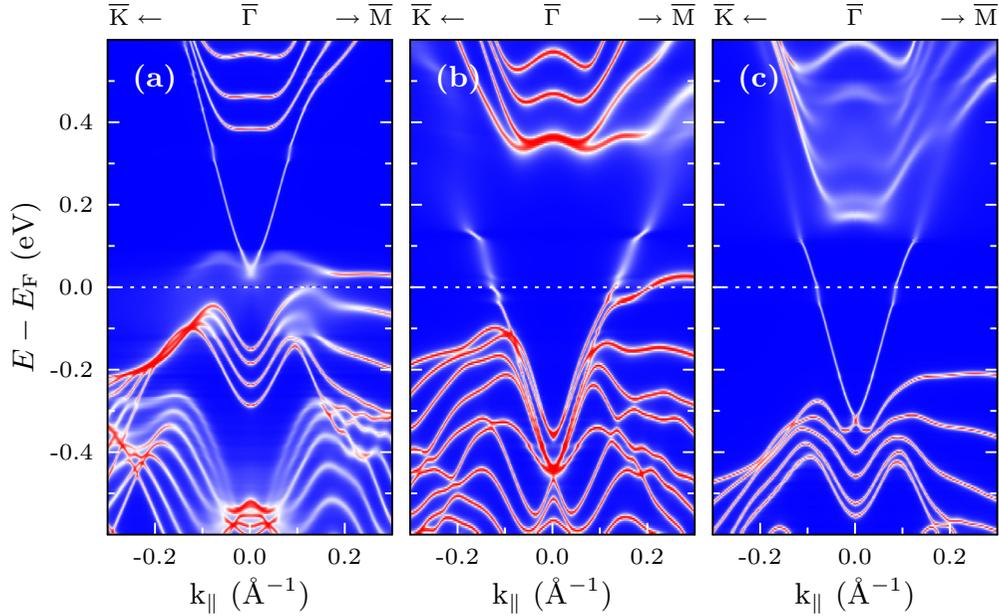


FIG. 2. The electronic structure of  $\text{Bi}_2\text{Se}_3(0001)$  calculated for different structure models: (a) Au in substitutional sites, (b) AuSe complexes on the  $\text{Bi}_2\text{Se}_3$  surface, and (c) AuSe complexes embedded into the  $\text{Bi}_2\text{Se}_3$  surface.

The Comment [2] does not refer to the second major experimental and theoretical part of the publication, namely, the experimental photoemission spectra shown in Fig. 3 and the theoretical spectra shown in Fig. 4 of Ref. [1]. The experimental spectra are almost perfectly reproduced by the calculation of the band structure, which exactly takes into account the Au substitutional site model.

In the following, we compare the band structures calculated for (i) the structural model with Au substituting Bi [1], (ii) the model with Se-Au-Se chains orientated randomly [2], and (iii) the model in which the Se-Au-Se structural unit is embedded into the surface. The last case was not discussed in the Comment [2], but this demonstrates how sensitively the band structure depends on the structure model. The calculations were carried out with the same methodology [12–14] as used in Ref. [1]. The amount of Au was set to 0.05 ML. The Se-Au-Se unit was constructed using the structural data taken from Ref. [15]. In the model (ii), Au atoms were assumed

to occupy the hcp hollow site, while Se atoms were placed either in the Au plane in the fcc hollow sites or outside the Au plane. In the model (iii), the same Se-Au-Se structural unit was embedded into the surface with Au replacing surface Se atoms. We have carried out the randomization of the Se-Au-Se structural unit within the surface plane using the coherent potential approximation [14,16].

The obtained results are shown in Fig. 2. As it was reported in our previous study [1], the presence of Au in Bi substitutional sites leads to opening the band gap [see Fig. 2(a)] in agreement with our photoemission measurements. This can be explained by the formation of Au impurity states of  $5d$  character [see Fig. 3(a)], which are located at the Fermi level and which penetrate deep into the bulk states significantly modifying the surface electronic structure [17–22]. There, the Dirac cone is not fully destroyed, which is also seen in the reported photoemission spectra [1]. Assuming the structural model with Se-Au-Se chains and carrying out

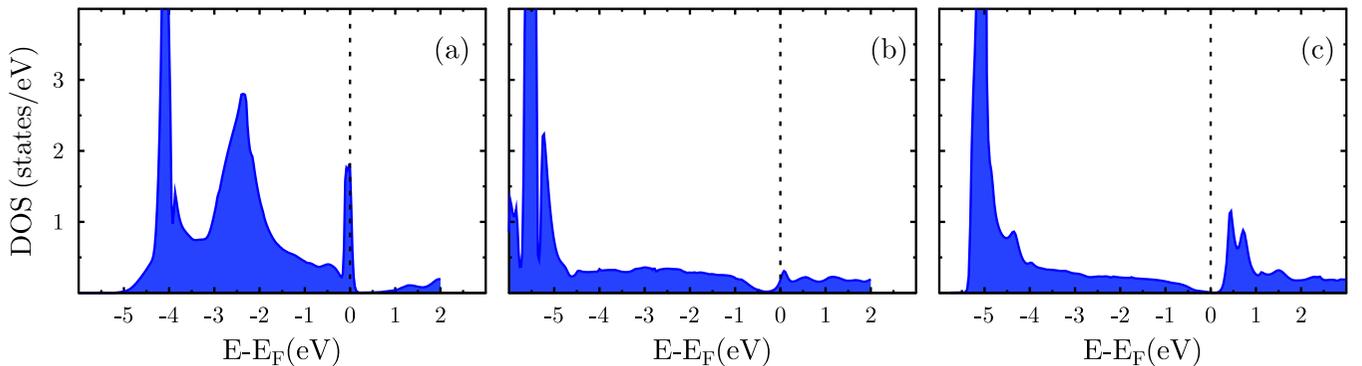


FIG. 3. The density of states of Au atoms in  $\text{Bi}_2\text{Se}_3(0001)$  calculated for different structure models: (a) Au in substitutional sites, (b) AuSe complexes on the  $\text{Bi}_2\text{Se}_3$  surface, and (c) AuSe complexes embedded into the  $\text{Bi}_2\text{Se}_3$  surface.

the domain averaging, we find a strong modification of the surface band structure [see Fig. 2(b)]. The Dirac cone is completely destroyed due to the presence of Au-*sp* states at the Fermi level [see Fig. 3(b)]. The related states are shifted down in energy into the bulk states. This is not observed in the photoemission experiment (see Fig. 3 in Ref. [1]). Thus we can exclude the formation of Se-Au-Se

structural units on the Bi<sub>2</sub>Se<sub>3</sub>(0001) surface. Embedding of the complexes into the surface QL neither destroys the Dirac cone nor does it lead to an opening of the band gap [see Fig. 2(c)], which also contradicts our experimental observation. In this case, Au *sp* states are located above the Fermi level [Fig. 3(c)] and thus only marginally affect the surface state.

- 
- [1] A. Polyakov, C. Tusche, M. Ellguth, E. D. Crozier, K. Mohseni, M. M. Otrokov, X. Zubizarreta, M. G. Vergniory, M. Geilhufe, E. V. Chulkov *et al.*, *Phys. Rev. B* **95**, 180202(R) (2017).
- [2] R. A. Gordon, *Phys. Rev. B* **98**, 136201 (2018).
- [3] X. Kou, M. Lang, Y. Fan, Y. Jiang, T. Nie, J. Zhang, W. Jiang, Y. Wang, Y. Yao, L. He *et al.*, *ACS Nano* **7**, 9205 (2013).
- [4] C.-Z. Chang, P. Tang, Y.-L. Wang, X. Feng, K. Li, Z. Zhang, Y. Wang, L.-L. Wang, X. Chen, C. Liu *et al.*, *Phys. Rev. Lett.* **112**, 056801 (2014).
- [5] A. I. Figueroa, G. van der Laan, L. J. Collins-McIntyre, S.-L. Zhang, A. A. Baker, S. E. Harrison, P. Schönerr, G. Cibin, and T. Hesjedal, *Phys. Rev. B* **90**, 134402 (2014).
- [6] Z. Liu, X. Wei, J. Wang, H. Pan, F. Ji, F. Xi, J. Zhang, T. Hu, S. Zhang, Z. Jiang *et al.*, *Phys. Rev. B* **90**, 094107 (2014).
- [7] A. I. Figueroa, G. van der Laan, L. J. Collins-McIntyre, G. Cibin, A. J. Dent, and T. Hesjedal, *J. Phys. Chem. C* **119**, 17344 (2015).
- [8] R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B* **25**, 925 (1969).
- [9] R. D. Shannon, *Acta Crystallogr., Sect. A* **32**, 751 (1976).
- [10] P. Larson and W. R. L. Lambrecht, *Phys. Rev. B* **78**, 195207 (2008).
- [11] S. C. Abrahams, *Acta Crystallogr., Sect. A* **25**, 165 (1969).
- [12] M. Lüders, A. Ernst, W. M. Temmerman, Z. Szotek, and P. J. Durham, *J. Phys.: Condens. Matter* **13**, 8587 (2001).
- [13] M. Geilhufe, S. Achilles, M. A. Köbis, M. Arnold, I. Mertig, W. Hergert, and A. Ernst, *J. Phys.: Condens. Matter* **27**, 435202 (2015).
- [14] B. L. Gyorffy, *Phys. Rev. B* **5**, 2382 (1972).
- [15] A. Rabenau and H. Schulz, *J. Less-Common Met.* **48**, 89 (1976).
- [16] P. Soven, *Phys. Rev.* **156**, 809 (1967).
- [17] R. R. Biswas and A. V. Balatsky, *Phys. Rev. B* **81**, 233405 (2010).
- [18] A. M. Black-Schaffer and A. V. Balatsky, *Phys. Rev. B* **85**, 121103 (2012).
- [19] A. M. Black-Schaffer and A. V. Balatsky, *Phys. Rev. B* **86**, 115433 (2012).
- [20] T. Schlenk, M. Bianchi, M. Koleini, A. Eich, O. Pietzsch, T. O. Wehling, T. Frauenheim, A. Balatsky, J.-L. Mi, B. B. Iversen *et al.*, *Phys. Rev. Lett.* **110**, 126804 (2013).
- [21] T. O. Wehling, A. M. Black-Schaffer, and A. V. Balatsky, *Adv. Phys.* **63**, 1 (2014).
- [22] P. Sessi, R. R. Biswas, T. Bathon, O. Storz, S. Wilfert, A. Barla, K. A. Kokh, O. E. Tereshchenko, K. Fauth, M. Bode *et al.*, *Nat. Commun.* **7**, 12027 (2016).