PHYSICAL REVIEW B **98**, 136201 (2018)

Comment on “Instability of the topological surface state in Bi_2Se_3 upon deposition of gold”

Robert A. Gordon[*]
Moyie Institute and Department of Physics, Simon Fraser University, Burnaby, BC, Canada V5A 1S6

(Received 23 August 2017; published 31 October 2018)

Polyakov *et al.* [Phys. Rev. B **95**, 180202(R) (2017)] have presented a comparison of experimental versus calculated photoemission for gold deposited on Bi_2Se_3, with the calculation based on a substitutional model of gold replacing bismuth, derived from an extended x-ray absorption fine-structure (EXAFS) analysis of the gold $L_{\rm III}$ edge. This Comment examines the coordination environment of gold in solid-state selenides in comparison to the model used, deficiencies within the EXAFS treatment presented by Polyakov *et al.*, and provides a more thorough examination and interpretation of the x-ray absorption near-edge structure (XANES) and the EXAFS that invalidates the claims by the authors of gold being substitutional in topological insulator Bi_2Se_3.

DOI: 10.1103/PhysRevB.98.136201

Polyakov *et al.* [1] have presented a comparison of experimental versus calculated photoemission for gold deposited on Bi_2Se_3, with the calculation based on a substitutional model of gold replacing bismuth. The photoemission data are highly diffuse and could not provide a definitive answer as to the local environment of the deposited gold. Extended x-ray absorption fine-structure (EXAFS) data were fit to a model with a gold atom in the bismuth position with three closer and three further nearest neighbors. This is a highly unusual coordination environment for gold in a selenide and warrants careful examination as to its uniqueness. This comment examines the coordination environment of gold in solid-state selenides in comparison to the model used, deficiencies within the EXAFS treatment presented therein, and provides a more thorough examination and interpretation of the x-ray absorption near-edge structure (XANES) and the EXAFS that invalidates the claims by the authors of gold being substitutional in topological insulator Bi_2Se_3.

Presented in Table I is a list of gold-containing inorganic selenides gleaned from the Inorganic Crystal Structure Database. Most are either 2-coordinate (linear) gold(I) or 4-coordinate (square-planar) gold(III). While exceptions to this are known within the coordination chemistry of gold [2–4], it is a very strong trend, and the three-coordinate (or distorted 6-coordinate) environment of the proposed gold substitution in bismuth selenide deviates from it. Bond lengths have a trend with monovalent two-coordinate bonds being shorter than trivalent 4-coordinate bonds. At 2.45 Å, the result of Polyakov *et al.* is borderline and not definitive.

Electron transfer from gold to the bismuth selenide was not addressed by Polyakov *et al.* If Au substitutes for Bi^{3+}, then Au^{3+} is a reasonable expectation, however, the XANES spectra of gold(III) species possess a pronounced peak at the edge [3,22] due to unoccupied $5d$ states. Figure 1 compares the normalized gold $L_{\rm III}$-edge XANES [23] with Au_2S and $AuCl_3$ [3], as representatives of gold(I) and gold(III), respectively, and their first derivatives. Note, the measured XANES spectra for the deposited film effectively overlap after normalization, suggesting isotropy or pseudoisotropy of the Au environment. XANES is used for its sensitivity to chemical speciation—local coordination and electron transfer (i.e., valence), and is often analyzed by comparison to known standards. The large peak in the near edge for Au(III) compounds is in sharp contrast to the weaker features for the linearly coordinated Au(I) in Au_2S, and other linearly coordinated Au(I) species [22]. The large peak (also known as a white line) for Au(III) is an indication of a substantial number of unoccupied $5d$ states on the gold. XANES of gold(I) with exceptions (with nonlinear gold coordination) noted above [3,4] all possess a peak in the near edge, indicating that $5d$ states are involved in bonding. For the deposited film data, there is no near-edge peak feature that would indicate that the $5d$ states are not fully occupied. The similarities between the deposited gold and linearly coordinated Au in Au_2S are quite pronounced, suggesting that electron transfer has resulted in a gold(I) species for the gold deposited on Bi_2Se_3 with linear coordination likely. This should serve as guide for fitting the EXAFS data to a model.

An EXAFS treatment requires generating a model calculation of the EXAFS interference function $\chi(k)$ with k the photoelectron momentum, using (omitting higher-order cumulants) the equation

$$\chi_{\rm model}(k) = \sum_j \frac{N_j^* S_o^2 F_j(k)}{kR_j^2} e^{-2\sigma_j^2 k^2} e^{\frac{-2R_j}{\lambda}} \times \sin[2kR_j + \delta_j(k)], \quad (1)$$

where potential fit parameters for the jth shell are the effective number of atoms N^* at distance R, with mean-square-relative displacement (msrd) σ^2. Since the measurements involved an orientation of the x-ray electric field perpendicular to the plane of the substrate and one orientation in the plane of the substrate, N^* is the effective polarization-dependent coordination number. For an $L_{\rm III}$ edge, the interpretation of N^* differs from that for a K edge [24] owing to contributions from transitions from $2p_{3/2}$ states to states with s character and states with

---

[*] ragordon@alumni.sfu.ca

2469-9950/2018/98(13)/136201(4)

TABLE I. List of inorganic gold-selenide compounds, formal gold valences therein, and nearest-neighbor (NN) distances.

Compound	Au Valence	NN (Å)	Reference
α-AuSe	+1	Se@2.418, 2.426	[5]
(2 Au sites)	+3	2Se@2.476, 2Se@2.497	
β-AuSe	+1	2Se@2.430	[5]
(2 Au sites)	+3	4Se@2.492	
NaAuSe	+1	2Se@2.457	[6]
KAuSe	+1	2Se@2.414	[7]
RbAuSe	+1	2Se@2.410	[8]
CsAuSe	+1	2Se@2.411	[9]
$NaAuSe_2$	+3	Se@2.459, 2.460, 2.489, 2.508	[10]
$KAuSe_2$	+3	4Se@2.476	[10]
$CsAuSe_3$	+1	2Se@2.401	[10]
AuSeBr	+3	2Se@2.448, 2Se@2.463	[11]
(2 Au sites)	+3	2Se@2.486, 2Se@2.491	
$RbAu_3Se_2$	+1	2Se@2.448	[12]
$CsAu_3Se_2$	+1	2Se@2.434	[12]
K_3AuSe_2	+1	2Se@2.411	[13]
Ag_3AuSe_2	+1	2Se@2.568	[14]
$AuCuSe_4$	+3	2Se@2.475, 2Se@2.483	[15]
$KAuSe_5$	+1	2Se@2.410	[16]
$Cs_2Au_2Se_3$	+1	Se@2.402, 2.404	[17]
$K_2Au_2Sn_2Se_6$	+1	2Se@2.433	[18]
$BaGdAuSe_3$	+1	2Se@2.576, 2Se@2.646	[19]
Tl_4AuSe_3	+2	2Se@3.134, 4Se@3.272	[20]
$K_3Au(Se_5)_2(Se_3)$	+3	2Se@2.464, 2Se@2.485	[16]
$Tl_2Au_2P_2Se_6$	+1	2Se@2.415	[21]
$Au{:}Bi_2Se_3$	?	3Se@2.45, 3Se@2.65	[1]

d character. In addition to these fit parameters, there is an energy shift parameter $\Delta E_{o,j}$ (often taken as the same for all shells) and S_o^2, which serves as an overall scale factor. Other values (scattering amplitude *F*, mean free path λ, phase shift δ) are obtained for the model calculation using a program such as FEFF [25]. The Debye-Waller term, $\exp(-2\sigma^2 k^2)$, has a *k*-dependent effect on amplitude and can be strongly correlated with the number of atoms in that shell. The number of atoms is also correlated with the overall scale (S_o^2). For a single shell, the correlation is 100%, and, as a consequence, one cannot vary both when trying to achieve a best fit. To correct for errors in scaling either from data normalization, an incorrect value of S_o^2, defects in coordination, or an incorrect structural model, one must vary a parameter (S_o^2 or *N*) that can scale independent of photoelectron momentum. In fitting to the substitution model, Polyakov *et al.* fixed both S_o^2 and *N*'s.

The fit detailed in Polyakov *et al.* was done assuming a split first peak with S_o^2 fixed at 0.8 and *N*'s fixed according to the substitutional model. The choice of $S_o^2 = 0.8$ is not unreasonable. Song *et al.* [22] found values between 0.76(5) and 0.85(5) for a number of standards. The problem in the fits is evident in the msrds for the second path in the split peak fit when compared to the value for the first path. Such a large difference, and associated lower-weighted contribution of the second path, suggests a single-shell fit would be better.

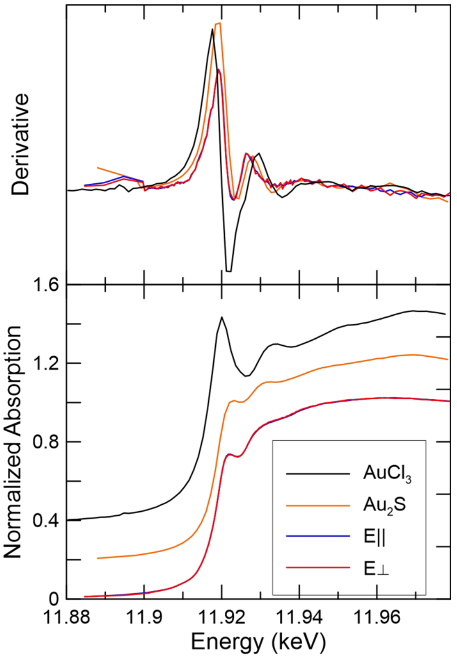

FIG. 1. Comparison of Au L_{III} XANES spectra (color online) and first derivatives for gold deposited on Bi_2Se_3 (two polarizations, overlapping), $AuCl_3$, and Au_2S, a linearly coordinated gold(I) compound.

One can undertake single-shell fits to the first peak—taking the same *k*-space range for $\chi(k)$ as in Fig. 1 of Polyakov *et al.* (i.e., ~3.78 to 12.05 Å^{-1}) with k^2 weighting and 10% Gaussian window function to transform to *R* space. Fits were done with WINXAS [26] in *R* space over the region of the first peak from 1.55 to 2.70 Å using amplitudes and phases (i.e., *F*, λ, δ) from the same starting model of Au on a Bi site in Bi_2Se_3. A comparison of data and single shell fits are shown in Fig. 2. Fit results are summarized in Table II. With residuals near 1.5%, both fits are an improvement over those reported by Polyakov *et al.* The distances obtained are comparable to many of the gold(I) nearest-neighbor distances

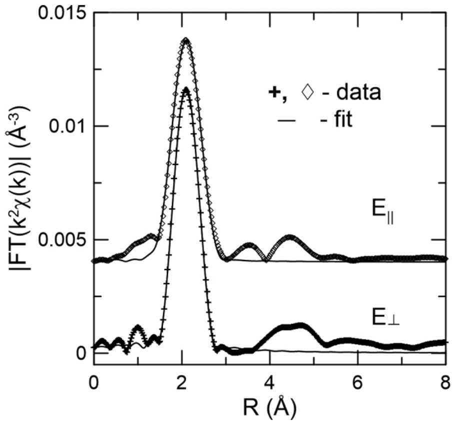

FIG. 2. Magnitude of k^2-weighted Fourier transforms (symbols) and associated single-shell fit results (line) of both in-plane and out-of-plane orientations for EXAFS measurements on gold deposited on Bi_2Se_3.

TABLE II. Single-shell fits results for both in-plane (∥) and out-of-plane (⊥) x-ray polarizations. Scaling (S_o^2) was fixed at 0.8. Errors were estimated by adjusting the parameter while others were fixed until the residual (Ru) exceeded 3%.

Pol.	$E_{\|\|}$	$E_\perp$
Shell	Se	Se
N^*	1.80(5)	2.03(5)
R (Å)	2.427(5)	2.425(5)
σ^2(Å^2)	0.0015(2)	0.0022(2)
ΔE_o(eV)	2.0(9)	1.9(9)
R_u(%)	1.5	1.4

listed in Table I. The effective coordination numbers are near 2. For a linearly coordinated gold(I) species, based on the equations of Citrin [24], effective coordination values could range from ∼1.4 if the polarization vector were normal to the Se-Au-Se chain, to ∼3.2 if parallel to the chain. Both N^* values obtained here are within that range. In fact, if the chains were randomly oriented, e.g., from formation of a second phase not commensurate with the substrate lattice, then the effective coordination number would be ∼2. An effective coordination number near 2 could also result if the nucleating phase were high symmetry (i.e., cubic similar to Au_2S). Such cases, or between these extremes, would also give rise to pseudoisotropy in the XANES as noted above. The result for the polarization in the plane of the substrate has both N^* and msrd lower than for the perpendicular orientation. This could be due in part to the correlation between N^* and msrd in achieving a best fit, in addition to some polarization dependence. The msrd values, however, are comparable to those reported by Song *et al.* [22]. Overall, the results are similar for the two orientations and consistent with a linearly coordinated gold(I) species.

Could the gold be present elsewhere in the Bi_2Se_3 structure and be consistent with the XANES and first shell fit results? One possibility is if the gold were interstitial between two selenium atoms. An examination of Se-Se distances in the Bi_2Se_3 structure [27] indicates the closest Se-Se distance values to twice the fit result (∼4.85 Å) are 4.23 and 5.43 Å. Accommodating gold as an interstitial between two Se atoms would then require a significant structural modification. There is a Se-Bi distance near 4.825 Å, but the fit does not indicate Bi is present in the first shell, so for this site to be considered, a number of antisite defects of the level of the film coverage would be necessary and require a significant structural modification. A third possibility is if the correlation between N^* and the msrd is obscuring a higher coordination. Trigonal planar geometry (threefold coordination) could be consistent with the absence of a significant number of empty d states as indicated by the XANES (i.e., sp^2 does not involve d states). Such sites as the surface hollow sites indicated in Fig. 2 of Polyakov *et al.* would allow such geometry. A consideration of effective coordination numbers [24] for trigonal planar geometry yields ∼2.1 for out-of-plane polarization, which is comparable to the fit value obtained, but also yields ∼3.45 for the in-plane polarization, which is substantially larger than the best fit value (note: to get the correct bond length, the Au would have to sit slightly above the plane, lowering the effective N to ∼3.4). Figure 3 examines the goodness of fit and msrd as a function of effective coordination number for fits to the in-plane data. At the 3% residual level, the single-shell fit quality is becoming visibly poor. For an $N^* \sim 3.45$, the goodness of fit is near 7.5%, well outside an acceptable fit result. This indicates that correlation between N^* and msrd is not obscuring potential threefold hollow site occupation. The Bi_2Se_3 structure does not appear able to accommodate the gold in a manner consistent with the XANES and EXAFS fit results without significant structural modification, which is tantamount to formation of a second phase (different structure and composition) with gold linearly coordinated by two selenium atoms.

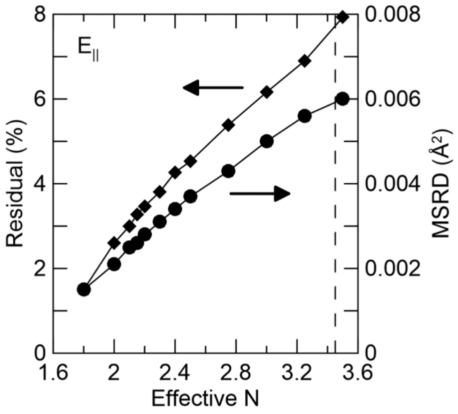

FIG. 3. Dependence of fit residual and mean-square-relative displacement on effective coordination number for the in-plane polarization data. The vertical dashed line indicates a calculated N^* value for in-plane trigonal planar geometry.

XANES indicates a gold(I) species is present. Single-shell fit results indicate gold is two-coordinate with a bond length consistent with other linearly coordinated gold(I) selenide compounds. The Bi_2Se_3 structure cannot accommodate this in a manner consistent with the data. This is not a substitution of gold for bismuth. This is evidence for a surface reaction on deposition resulting in the formation of a second phase with linear gold coordination.

---

[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, A. Ernst, H. L. Meyerheim, and S. S. P. Parkin, Phys. Rev. B **95**, 180202(R) (2017).

[2] M. Concepción Gimeno, in *Modern Supramolecular Gold Chemistry: Gold-Metal Interactions and Applications*, edited by A. Laguna (WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008), Chap. 1.

[3] L. J. Cabri, M. Newville, R. A. Gordon, E. D. Crozier, S. R. Sutton, G. McMahon, and D.-T. Jiang, Can. Mineral. **38**, 1265 (2000).

[4] T. Bartsch, O. Niehaus, D. Johrendt, Y. Kobayashi, M. Seto, P. M. Abdala, M. Bartsch, H. Zacharias, R.-D. Hoffmann, B. Gerke, U. Ch. Rodewald, and R. Pöttgen, Dalton Trans. **44**, 5854 (2015).
[5] A. Rabenau and H. Schulz, J. Less-Common Met. **48**, 89 (1976).
[6] K. O. Klepp, J. Alloys Compd. **234**, 199 (1996).
[7] K. O. Klepp and W. Bronger, J. Less-Common Met. **128**, 65 (1987).
[8] K. O. Klepp and C. Weithaler, Z. Kristallogr. **211**, 549 (1996).
[9] W. Bronger and H. U. Kathage, J. Alloys Compd. **184**, 87 (1992).
[10] Y. Park and M. G. Kanatzidis, J. Alloys Compd. **257**, 137 (1997).
[11] D. Mootz, A. Rabenau, H. Wunderlich, and G. Rosenstein, J. Solid State Chem. **6**, 583 (1973).
[12] K. O. Klepp and C. Weithaler, J. Alloys Compd. **243**, 1 (1996).
[13] K. O. Klepp and C. Weithaler, Z. Kristallogr. **210**, 221 (1995).
[14] P. Messien and M. Baiwir, Bull. Soc. R. Sci. Liège **35**, 234 (1966).
[15] Y. Park and M. G. Kanatzidis, Inorg. Chem. **40**, 5913 (2001).
[16] Y. Park and M. G. Kanatzidis, Angew. Chem. **102**, 945 (1990).
[17] K. O. Klepp and C. Weithaler, Eur. J. Sol. State Inor. **35**, 101 (1998).
[18] S. Loeken and W. Tremel, Z. Anorg. Allg. Chem. **624**, 1588 (1998).
[19] Y. T. Yang and J. A. Ibers, J. Solid State Chem. **147**, 366 (1999).
[20] T. Doert, S. Hoffkes, C. Klein and P. Boettcher, Z. Kristallogr. Suppl. Issue **3**, 52 (1991).
[21] M. A. McGuire, T. K. Reynolds and F. J. DiSalvo, Chem. Mater. **17**, 2875 (2005).
[22] Z. Song, J. P. L. Kenney, J. B. Fein, and B. Bunker, Geochim. Cosmochim. Acta **86**, 103 (2012).
[23] The same data as used in Polyakov *et al.* used with permission.
[24] P. H. Citrin, Phys. Rev. B **31**, 700 (1985).
[25] S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers, and M. J. Eller, Phys. Rev. B **52**, 2995 (1995).
[26] T. Ressler, J. Phys. IV France **7**, C2-269 (1997).
[27] S. Nakajima, J. Phys. Chem. Solids **24**, 479 (1963).