New Layered Structures of Cuprous Chalcogenides as Thin Film Solar Cell Materials: Cu_2Te and Cu_2Se

Manh Cuong Nguyen,[1] Jin-Ho Choi,[2] Xin Zhao,[1] Cai-Zhuang Wang,[1] Zhenyu Zhang,[2,*] and Kai-Ming Ho[1,2,†]

[1]*Ames Laboratory–US DOE and Department of Physics and Astronomy,*
Iowa State University, Ames, Iowa 50011, USA
[2]*International Center for Quantum Design of Functional Materials (ICQD),*
Hefei National Laboratory for Physical Sciences at the Microscale,
University of Science and Technology of China, Hefei, Anhui 230026, China

(Received 27 March 2013; revised manuscript received 9 August 2013; published 15 October 2013)

The stable crystal structures of two cuprous chalcogenides of Cu_2X (X = Te or Se) are predicted using an adaptive genetic algorithm in combination with first-principles density functional theory calculations. Both systems are found to prefer a unique and previously unrecognized layered structure, with the total energies much lower than all structures proposed in the literature so far. The newly discovered structures are further shown to be dynamically and mechanically stable, and possess electronic properties consistent with existing experimental observations. In particular, their layered nature is expected to prevail over other structural forms at the interfaces of thin-film solar cells, and knowledge about the precise atomic structures of the interfaces is a prerequisite for achieving long-term stability and high efficiency of CdTe and Cu(In, Ga)Se_2 solar cells.

DOI: 10.1103/PhysRevLett.111.165502 PACS numbers: 61.50.−f, 63.20.D−, 68.55.−a

CdTe thin-film solar cells have been regarded as one of the most promising classes of solar cells; nevertheless, the conversion efficiency of the CdTe-based solar cells has been increased by only ~1.5% (from 15.8% to 17.3%) over the past 10 years [1,2]. The long-term instability issues characterized by significant efficiency loss with performance duration [3] also remain unsolved. In these thin-film solar cell devices, Cu_2Te is one of the most commonly used back-contact materials, and the diffusion of Cu atoms into the absorber layer causes the degradation of the CdTe solar cells. Thus, knowledge about the interface structures at the atomic level is a prerequisite for solving this standing issue and further improving the conversion efficiency.

Two low-temperature crystalline phases of Cu_2Te have been proposed experimentally, the hexagonal structure [4] and the orthorhombic superstructure with a much larger unit cell [5,6]. For the orthorhombic superstructure, only the lattice parameters have been determined experimentally [5,6], while the detailed atomic positions of this superstructure remain unsolved. For the simpler hexagonal phase, a structural model was proposed by Nowotny about 70 years ago [4]. However, a recent theoretical study using first-principles density functional theory (DFT) calculations showed that the Nowotny model structure is energetically unfavorable [7]. Several alternative structural models have also been proposed based on the DFT study [7], but none of these candidate structures is energetically favorable either. Thus, the correct structural models for Cu_2Te are still unavailable.

Going from Te to Se, Cu_2Se is also important for the synthesis of another popular class of thin-film solar cells: Cu(In, Ga)Se_2 (CIGS). Again, the atomic structure is unclear. Various experiments [8–10] have been performed to determine the crystal structure of the low-temperature Cu_2Se phase. However, most of the experimental studies have been focused on determining the lattice parameters, rather than the detailed atomic positions. One exception was the recent x-ray diffraction study [10], which proposed a crystal structural model for the low-temperature Cu_2Se phase with a very large and complex unit cell containing 144 atoms. Moreover, even the lattice parameters proposed from different experimental studies are highly controversial [8–10]. Reliable theoretical efforts on determination of the crystal structures are also lacking for both Cu_2Se and Cu_2Te.

In this Letter, on the basis of the adaptive genetic algorithm (AGA) combined with first-principles DFT calculations, we present novel structural models for the two cuprous chalcogenide compounds, Cu_2Te and Cu_2Se. We find that both systems prefer layered structures with lower total energies than those of the structural models reported previously. The new structural model for Cu_2Te is much more stable than the Nowotny model structure, by −530.0 meV per formula unit (f.u.). For Cu_2Se, the newly discovered layered structure is also lower in total energy than the previous model, by −28.25 meV/f.u. Detailed calculations of the phonon band structure and elastic constants further show that the new structural models are dynamically and mechanically stable. Given the significant gains in the total energy and their layered nature, we expect that the new structures for Cu_2Te and Cu_2Se can occur at the interfaces of the Cu back contacts with various semiconductor substrates. Identification of the precise stable structures of these elemental materials provides valuable crystal structural

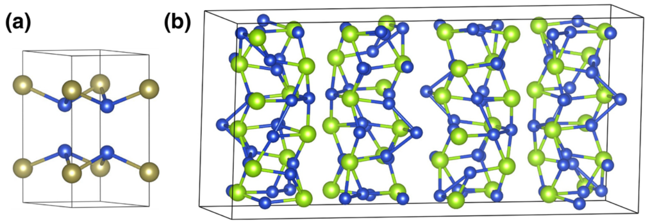

FIG. 1 (color online). (a) The Cu_2Te Nowotny structure, and (b) the recently proposed Cu_2Se structure, with the unit cells shown by the solid lines. The larger (golden or green) spheres are the chalcogen atoms (Te or Se), and the smaller (blue) spheres are the Cu atoms.

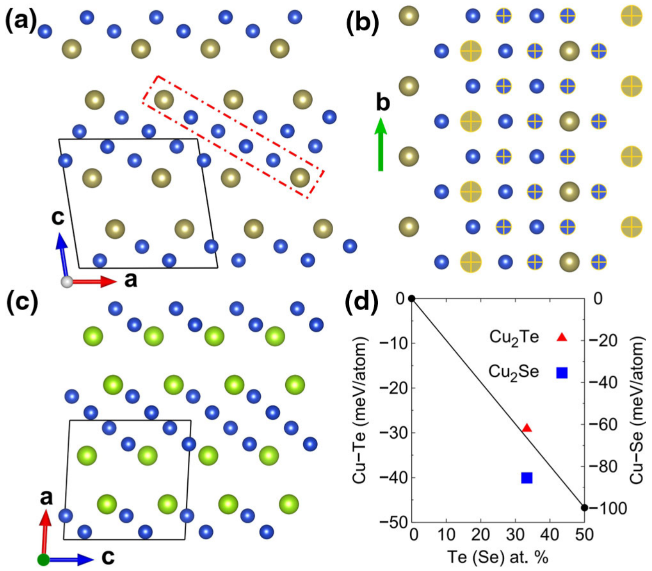

FIG. 2 (color online). The lowest energy structures of (a) Cu_2Te and (c) Cu_2Se with the unit cells shown by the solid lines. (b) Top view of two adjacent ribbons from a Cu_2Te "layer." (d) The relative formation energy of Cu_2Te (Cu_2Se) with respect to the fcc Cu and bulk Te (Se) structures. In (b), the crossed spheres indicate atoms from the back ribbon.

information for fundamental and applied studies of a wide variety of thin-film solar cell materials and devices.

As starting reference models, the Nowotny structure for Cu_2Te and the recently proposed structure for Cu_2Se are illustrated in Fig. 1. We performed global crystal structure searches for the two cuprous chalcogenides of Cu_2Te and Cu_2Se by the recently developed adaptive genetic algorithm [11,12], adopting unit cells up to 8 f.u. All searches were "from scratch": the chemical compositions were the only given information, no crystal shapes were assumed and the initial atomic positions in the unit cells were randomly generated. The "auxiliary" classical potentials used in our AGA search were based on the embedded atom method (EAM) [13]. The local structural optimizations within the "auxiliary" classical potential scheme were carried out using the LAMMPS code [14]. First-principles DFT [15] calculations were performed within the local density approximation (LDA) [16] and the projector-augmented wave pseudopotential method [17,18], as implemented in the VASP code [19]. The kinetic energy cutoff in the DFT calculations was set to 370 eV and the Monkhorst-Pack's scheme [20] was used for k-point sampling. A k-point mesh of $5 \times 11 \times 6$ ($6 \times 10 \times 6$) was employed for the calculations with the Cu_2Te (Cu_2Se) structure proposed below. Similar high-quality k-point meshes were employed for all other calculations. The references for the formation energy calculations are the ground-state structures of Cu, Te, and Se, which are face-centered cubic Cu, $P3_121$ Te, and $P3_121$ Se structures, respectively.

We chose the Cu EAM potential developed by Zhou *et al.* [21] for pure Cu components and fitted the crossing-pair interactions and pure Te or Se components of the binary alloy EAM potentials. We also tried to fit all the functions (including the pure Cu components as well) in some searches. We used the Morse or Lennard-Jones function for pair interactions, exponential decaying functions for electron density, and the function proposed by Banerjea *et al.* [22] as embedding energy functions. The EAM potentials were fitted to the DFT energies, forces, and stresses by the force-matching method [23] implemented in the potfit code [24,25], using the stochastic simulated annealing algorithm [26] for minimization. To investigate the dynamical stability of the obtained structures, we calculated the phonon frequencies throughout the Brillouin zone, using the finite displacement method [27] implemented in the PHONOPY code [28]. More details about the AGA method are given in the Supplemental Material [29].

The lowest-energy structures of Cu_2Te and Cu_2Se obtained from our AGA searches are shown in Fig. 2, together with their unit cells indicated by the solid lines. We first discuss in detail the lowest-energy structure of Cu_2Te [Figs. 2(a) and 2(b)]. It is a monoclinic (space group $C2/m$) structure including 4 Cu_2Te f.u. in a unit cell. The optimized lattice parameters are $a = 7.693$ Å, $b = 3.803$ Å, $c = 7.248$ Å, $\alpha = 90.00°$, $\beta = 98.88°$, and $\gamma = 90.00°$. The basis Cu atoms occupy 2 different $4i$ Wyckoff positions: Cu1 (−0.02264, 0, 0.16652) and Cu2 (−0.34211, 0, 0.05893), and the basis Te atom occupies a third $4i$ Wyckoff position: Te (0.30385, 0, 0.30249). The total energy of this new structure is −530.0 and −155.0 meV/f.u. lower than that of the Nowotny model and the recently proposed model by Da Silva *et al.* [7], respectively. It is notable that the lowest-energy structure reported previously [7] still has a positive formation energy of +67 meV/f.u., indicating its energetically unstable nature, while the new structure is favorable with a negative formation energy of −88.0 meV/f.u.

The new Cu_2Te structure possesses the Te-terminated layered structure (hereafter "layer"), as shown clearly in Fig. 2(a). The terminating Te layer is a stretched hexagonal lattice with parameters of $a = 4.29$ Å and $\gamma = 52.62°$, which are quite close to those of the CdTe (111) surface: $a = 4.53$ Å and $\gamma = 60°$. The "layer" width of the new Cu_2Te structure is 4.33 Å and the gap between two adjacent "layers" is 2.83 Å. It is noticeable that each Cu_2Te "layer" consists of Cu_2Te ribbons, marked by the dot-dashed rectangle in Fig. 2(a), tilted about 30° with respect to the terminating Te layer. The ribbon is in the direction of the lattice vector $\mathbf{b}$ and its width is 8.56 Å. The top view of two adjacent ribbons is displayed in Fig. 2(b). The ribbon possesses two Te lines at both edges and four inner Cu lines, equally spaced between the six lines. In the atomic lines, atoms are shifted by a half of the lattice vector $\mathbf{b}$, making the face-centered rectangle pattern of the ribbon. The length of the longer side of the rectangle is $|\mathbf{b}| = 3.80$ Å and that of the shorter one is $|\mathbf{a}'| = 3.46$ Å. The back ribbon is shifted from the front one by a vector $\mathbf{a}'$ and a half of the vector $\mathbf{b}$ on the ribbon plane, with a ribbon spacing of 1.87 Å, making a face-centered orthorhombic (fco) structure (if the ribbons' width is infinite) with parameters of $a' = 3.46$ Å, $b' = b = 3.80$ Å, and $c' = 3.74$ Å. This fco structure is distorted less than 8% from the fcc Cu bulk ($a = 3.46$ Å) structure, and therefore, showing the fcc-bulk-like arrangement of the Cu atoms. It is notable that the new Cu_2Te structure has the higher coordination numbers for the Cu atoms than those in the Nowotny model structure: the average Cu coordination number is 10 and 7 for the former and the latter, respectively. In contrast, the coordination numbers for the Te atoms are 6 for both structures. Therefore, the higher Cu coordination numbers may be the reason for the much lower formation energy of the new Cu_2Te structure than that of the Nowotny model.

The lowest-energy structure for the Cu_2Se compound [Fig. 2(c)] is also a monoclinic (space group $P2_1/c$) structure including 4 Cu_2Se f.u. in a unit cell, and its formation energy is -256.25 meV/f.u. This new structure is -328.09 and -28.25 meV/f.u. lower in total energy than the high temperature antifluorite structure [30] and the low-temperature one proposed in a recent x-ray study [10], respectively. The latter is a monoclinic structure (space group $C2/c$) with a unit cell consisting of 48 Cu_2Se f.u. We note that the new Cu_2Se structure also possesses Cu_2X ribbons adopting a near body-centered square pattern, similar to the new Cu_2Te structure [see Figs. 2(a) and 2(c)]. The noticeable structural differences between the new Cu_2Se and Cu_2Te structures are the different stacking of the Cu_2X ribbons and their b/a' ratios. The back ribbon of the new Cu_2Se structure is shifted by $(1/2 + 0.16)\mathbf{b}$, instead of $1/2\mathbf{b}$ in the case of Cu_2Te, along the ribbon direction from the front ribbon. The new Cu_2Se structure has a b/a' ratio of 1.56, which is 0.46 larger than that (1.10) of the new Cu_2Te, and the larger b/a' ratio can be explained by the difference in the covalent radii of a chalcogen atom and Cu, as discussed below. The detailed lattice parameters of the new Cu_2Se structure are as follows: $a = 6.554$ Å, $b = 4.201$ Å, $c = 6.660$ Å, $\alpha = 90.00°$, $\beta = 87.05°$, and $\gamma = 90.00°$. The basis Cu atoms occupy 2 different $4e$ Wyckoff positions: Cu1 (0.06444, -0.42110, 0.17094) and Cu2 (-0.19990, -0.07620, -0.00724). The basis Se atom occupies a third $4e$ Wyckoff position: Se (0.29649, -0.06260, 0.34271).

At this point, it is natural to question whether Cu_2S would also prefer a layered structure as its two electronically similar sister systems of Cu_2Se and Cu_2Te. We have also performed global crystal structure searches for Cu_2S bulk using the AGA method and found that the lowest-energy structure is not layered. To explain this difference, we note that the covalent radius of Te, Se, and S is ~0.03, ~0.22, and ~0.36 Å shorter than that of Cu, respectively. The much shorter covalent radius of S may cause strong strain in the ribbon structure, preventing the fcc-like structure of the Cu atoms and resulting in a relatively large b/a' ratio (1.40) in layered Cu_2S. Even though the b/a' ratio is slightly smaller than that of Cu_2Se, the Cu_2S structure shows much more pronounced distortions and ripples in the ribbon structure, indicating a higher strain energy cost than the other two Cu_2X structures. Indeed, the layered structure of Cu_2S exhibits large deviations in the Cu-Cu bond lengths by ~0.2 Å, while the other two Cu_2X structures show relatively uniform Cu-Cu bond lengths with a deviation of ~0.05 Å. Detailed comparisons will be presented elsewhere.

Going beyond the static energetic studies presented above, we perform phonon calculations throughout the Brillouin zones of the new Cu_2Te and Cu_2Se structures to investigate their dynamical stability. The phonon band structures in Fig. 3 demonstrate that both of the $C2/m$ Cu_2Te and $P2_1/c$ Cu_2Se structures are dynamically stable without any soft phonon mode. In addition, we have performed elastic constant calculations to investigate the mechanical stability of the newly found structures, and find that both the $C2/m$ Cu_2Te, and $P2_1/c$ Cu_2Se structures meet the mechanical stability criteria (see Supplemental Material [29] for more details). We thus conclude that the

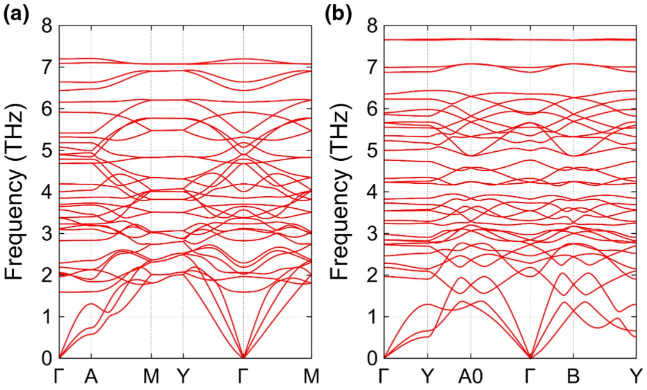

FIG. 3 (color online). Phonon band structure of the (a) $C2/m$ Cu_2Te and (b) $P2_1/c$ Cu_2Se structures.

newly found $C2/m$ Cu_2Te and $P2_1/c$ Cu_2Se structures are energetically, dynamically, and mechanically stable.

To further investigate the relative stabilities of the newly found structures with respect to the other well-known phases of Cu-Te and Cu-Se systems, we compare their formation energies with those of the $Pmmn$ CuTe [31], $P6_3/m$ CuSe [32] and fcc Cu structures [see Fig. 2(d)]. The formation energy of the $C2/m$ Cu_2Te structure is located only 2 meV/atom above the tie line connecting the fcc Cu and the $Pmmn$ CuTe structure. The very small energy difference of 2 meV/atom may imply that the structure can be stabilized when it is deposited on other semiconductor surfaces. In contrast, the formation energy of the $P2_1/c$ Cu_2Se structure is located below the tie line connecting the fcc Cu and the $P6_3/m$ CuSe, indicating stability of the new Cu_2Se against decomposition.

We have also investigated the electronic properties of the newly found Cu_2Te and Cu_2Se structures by performing band structure calculations. Here we used the modified Becke-Johnson (MBJ) potential scheme [33,34] for accurate band structure calculations. We find that $C2/m$ Cu_2Te has no band gap with small density of state at the Fermi level, while $P2_1/c$ Cu_2Se has a band gap of 0.74 eV. These results are consistent with the existing experimental observations, which showed that Cu_2Te is metallic [35,36] and Cu_2Se is semiconducting [37].

Before closing, we note that Cu_2Te or Cu_2Se layers are usually deposited on other semiconductor materials in the fabrication process of thin-film solar cells. For example, Cu_2Te layers are deposited as the back contact material on a light-absorbing CdTe layer. The structural phase of the deposited Cu_2Te or Cu_2Se could be different from the ground-state structure in the case of the bulk system, because of the interfacial interaction effect on the interface formation kinetics. Thus, the ordered and layered structures of the new Cu_2Te and Cu_2Se could have more advantages in forming the interface structures than other structural forms. In fact, we find that the new Cu_2Te and Cu_2Se structures have a relatively small (compared with typical chemical bindings) inter-"layer" binding energy of 118.0 and 101.1 meV per chalcogen, respectively, indicating easy separation of the "layer." In addition, we have examined the effect of van der Waals (vdW) interactions by performing DFT calculations within the van der Waals density functional (vdW-DF) scheme [38,39]. We find that the inclusion of the vdW interactions results in further decreases in the inter-"layer" distances X-X ($X =$ Te or Se), as well as slight increases in the surface energies compared to the local density approximation results. Quantitatively, the decrease (increase) in the interlayer distance (surface energy) is 0.23 Å (8.1 meV) and 0.28 Å (11.9 meV) for Cu_2Te and Cu_2Se, respectively. These results show that the vdW interactions can play a considerable role in the stacking and enhanced stabilization of the Cu_2X layers.

In summary, we have proposed novel structural models for the two cuprous chalcogenide compounds, Cu_2Te and Cu_2Se, using the AGA method combined with DFT calculations. The proposed structural models show Te- or Se-terminated layered structures consisting of Cu_2X ribbons. We found that the newly found Cu_2X structures are not only energetically more stable than the all known lowest-energy structures reported in the literature, but also dynamically and mechanically stable. Because of their overall stability and layered nature, the newly proposed Cu_2Te and Cu_2Se structures can be favorable on various semiconductor surfaces. Therefore, the new structural models may shed more light on the Cu_2X/semiconductor interfaces in thin-film solar cells and offer new opportunities for improving the overall performance of the CdTe and CIGS thin-film solar cells.

The U.S. Department of Energy, Office of Basic Energy Science, Division of Materials Science and Engineering supported the research, including GA development, at the Ames Laboratory, which is operated for the DOE by Iowa State University under Contract No. DE-AC02-07CH11358, with an additional computing grant through the National Energy Research Scientific Computing Center (NERSC). The work was also partially supported from Korea (J.-H. C., NRF Grant No. 2012R1A6A3A03040199) and China (J.-H. C. and Z. Z., NSFC Grants No. 11034006 and No. 11250110056). M. C. N. and J.-H. C. contributed equally to this work.

---

*zhangzy@ustc.edu.cn
†kmh@ameslab.gov

[1] X. Wu, S. Asher, D. H. Levi, D. E. King, Y. Yan, T. A. Gessert, and P. Sheldon, J. Appl. Phys. **89**, 4564 (2001).
[2] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop, Prog. Photovoltaics **20**, 606 (2012).
[3] K. D. Dobson, I. Visoly-Fisher, G. Hodes, and D. Cahen, Solar Energy Mater. Sol. Cells **62**, 295 (2000).
[4] H. Nowotny, Z. Metallkd. **37**, 40 (1946).
[5] I. Patzak, Z. Metallkd. **47**, 418 (1956).
[6] R. Blachnik, M. Lasocka, and U. Walbrecht, J. Solid State Chem. **48**, 431 (1983).
[7] J. L. F. Da Silva, S.-H. Wei, J. Zhou, and X. Wu, Appl. Phys. Lett. **91**, 091902 (2007).
[8] G. P. Sorokin, G. Z. Idrichan, Z. M. Sorokina, L. P. Kaptar, Inorg. Mater. (USSR) **10**, 1537 (1974).
[9] S. Kashida, W. Shimosaka, M. Mori, and D. Yoshimura, J. Phys. Chem. Solids **64**, 2357 (2003).
[10] L. Gulay, M. Daszkiewicz, O. M. Strok, and A. Pietraszko, Chem. Met. Alloys **4**, 200 (2011), and references therein.
[11] D. M. Deavon and K. M. Ho, Phys. Rev. Lett. **75**, 288 (1995).
[12] M. Ji, K. Umemoto, C.-Z. Wang, K.-M. Ho, and R. M. Wentzcovitch, Phys. Rev. B **84**, 220105 (2011).
[13] M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).
[14] S. Plimpton, J. Comput. Phys. **117**, 1 (1995).

[15] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[16] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[17] P. E. Blochl, Phys. Rev. B **50**, 17 953 (1994).
[18] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[19] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11 169 (1996); Comput. Mater. Sci. **6**, 15 (1996).
[20] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[21] X. W. Zhou, R. A. Johnson, and H. N. G. Wadley, Phys. Rev. B **69**, 144113 (2004).
[22] A. Banerjea and J. R. Smith, Phys. Rev. B **37**, 6632 (1988).
[23] F. Ercolessi and J. B. Adams, Europhys. Lett. **26**, 583 (1994).
[24] P. Brommer and F. Gahler, Model. Simul. Mater. Sci. Eng. **15**, 295 (2007).
[25] P. Brommer and F. Gahler, Philos. Mag. **86**, 753 (2006).
[26] S. Kirkpatrick, C. D. Gellat, and M. P. Vecchi, Science **220**, 671 (1983).
[27] K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett. **78**, 4063 (1997).
[28] A. Togo, F. Oba, and I. Tanaka, Phys. Rev. B **78**, 134106 (2008).
[29] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.111.165502 for more details of the adaptive genetic algorithm and mechanical properties of the newly found Cu_2Te and Cu_2Se structures.
[30] K. Yamamoto and S. Kashida, J. Solid State Chem. **93**, 202 (1991).
[31] R. V. Baranova, V. P. Aref'ev, and S. A. Semiletov, Inorg. Mater. (USSR) **13**, 1720 (1977).
[32] F. Lippmann, Neues Jahrb. Meneral., Monatsh. 99 (1962).
[33] A. D. Becke and E. R. Johnson, J. Chem. Phys. **124**, 221101 (2006).
[34] F. Tran and P. Blaha, Phys. Rev. Lett. **102**, 226401 (2009).
[35] S. Miyatani, S. Mori, and M. Yanagihara, J. Phys. Soc. Jpn. **47**, 1152 (1979).
[36] X. Wu, J. Zhou, A. Duda, Y. Yan, G. Teeter, S. Asher, W. K. Metzger, S. Demtsu, S.-H. Wei, and R. Noufi, Thin Solid Films **515**, 5798 (2007).
[37] G. B. Abdullaev, Z. A. Aliyarova, and G. A. Asadov, Phys. Status Solidi **21**, 461 (1967).
[38] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. **92**, 246401 (2004).
[39] G. Román-Pérez and J. M. Soler, Phys. Rev. Lett. **103**, 096102 (2009).