

The Effect of Spin–Orbit Coupling on the Surface Dynamical Properties and Electron–Phonon Interaction of Tl(0001)

I. Yu. Sklyadneva,^{†,‡,§} R. Heid,[§] K.-P. Bohnen,[§] P. M. Echenique,^{||} G. Benedek,^{†,⊥} and E. V. Chulkov^{*,||}

[†]Donostia International Physics Center (DIPC), P. de Manuel Lardizabal 4, 20080 San Sebastián/Donostia, Basque Country, Spain

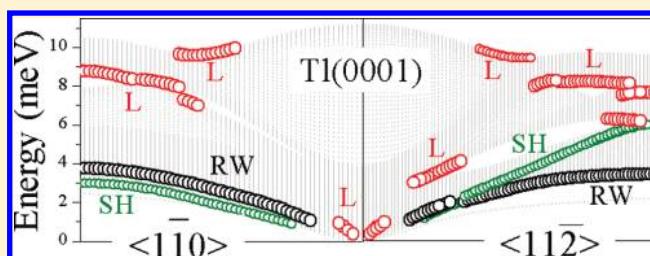
[‡]Institute of Strength Physics and Materials Science, pr. Akademicheskii 2/1, 634021 and Tomsk State University 634050 Tomsk, Russia

[§]Institut für Festkörperphysik, Karlsruher Institut für Technologie, D-76021 Karlsruhe, Germany

^{||}Departamento de Física de Materiales and Centro de Física de Materiales CFM - Materials Physics Center MPC, Centro Mixto CSIC-UPV/EHU, Facultad de Ciencias Químicas, UPV/EHU, Donostia International Physics Center (DIPC), Apdo. 1072, 20080 San Sebastián/Donostia, Basque Country, Spain

[⊥]Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Via Cozzi 53, 20125 Milano, Italy

ABSTRACT: We present an ab initio study of the effect of spin–orbit coupling on the dynamical properties of the Tl(0001) surface as well as on the electron–phonon interaction at the surface. The calculations based on density-functional theory were carried out using a linear response approach and a mixed-basis pseudopotential method. It is shown that the spin–orbit effects on the phonon spectrum and the electron–phonon interaction at the Fermi level of the surface are weak but conspire to a reduction in the electron–phonon coupling



I. INTRODUCTION

It is known that the spin–orbit (SO) coupling becomes more and more effective with increase of the nuclear charge. The SO coupling has been shown to have an important effect on structural and electronic properties of ultrathin films^{1–6} and surfaces^{4,7–11} of heavy metals as well as on bulk properties of these metals.^{12,13} The SO coupling also has a profound impact on lattice vibrations in bulk Bi¹⁴ and Pb^{13,15,16} as well as on electron–phonon (e–ph) interaction in Pb,¹⁶ while the influence of the SO interaction on the phonon frequencies and e–ph coupling of bulk Tl is rather weak.¹⁶ However, it is interesting to verify whether the effects of SO interaction on the phonon frequencies and e–ph coupling are enhanced at the Tl(0001) surface. This interest is also motivated by the fact that some systems show the enhancement of e–ph interaction on their surfaces compared to the bulk.^{17–20}

Thallium and its compounds are of particular scientific interest because of its superconductive properties and practical importance in high-technology fields.²¹ Due to its high toxicity, thallium has been less studied experimentally as compared to other 6-sp metals such as gold, lead, and bismuth. A great deal of experimental and theoretical information is now available on structural and electronic properties of well-ordered thin thallium overlayers formed on semiconductor surfaces such as Si(111) and Ge(111).^{22–26} However, this is not the case for thallium surfaces whose geometry and electronic structure are still poorly known. Regarding the lattice dynamics, experimental and

theoretical data are available only for bulk Tl.^{16,27} Its phonon band structure with and without the SO interaction has been studied using ab initio calculations¹⁶ within the density-functional perturbation theory, an efficient approach to provide information about the vibrational properties of a wide range of materials.^{28,29} The inclusion of the SO coupling was found to modify the bulk phonon frequencies by less than 0.2 meV throughout the whole Brillouin zone.

In this work we extend the study of the SO effects by examining their influence on the phonon structure of the Tl(0001) surface, which has not been studied before. We show that the SO-induced modifications of the phonon frequencies are only slightly larger than in the case of bulk Tl, but still of the order of 1%–2%. The exception is the Rayleigh mode at the surface Brillouin zone (SBZ) boundary, which is enhanced by more than 10% (0.2–0.3 meV). We have also evaluated the e–ph interaction at the Fermi level of the surface. We find that the e–ph coupling strength λ_{EF} is weakened by 16% when the SO interaction is taken into account.

The paper is organized as follows. A short outline of the calculation method is given in section II. Section III presents the

Special Issue: J. Peter Toennies Festschrift

Received: February 1, 2011

Revised: May 20, 2011

Published: May 23, 2011

results for the SO effects on the dynamical properties of the surface and the e–ph coupling. The conclusions are drawn in section IV.

II. DETAILS OF THE CALCULATION

The calculations have been performed within the density-functional perturbation theory²⁹ in a mixed-basis pseudopotential representation.^{30,31} Details of the SO implementation were reported in the previous paper.¹⁶ The norm-conserving scalar and fully relativistic pseudopotentials³² and the local density approximation for the exchange and correlation energy functional³³ are used together with a combination of local functions and plane waves for the representation of valence electronic states. Like in the case of bulk Tl,¹⁶ we use the pseudopotentials with *Sd* semicore states included. To treat the deep *d* potentials, *Sd*-type local functions at each atomic site are used to accelerate the convergence and at the same time to reduce the size of the plane wave basis set for which a cutoff of 20 Ry is found to be enough. SBZ integrations are performed with a uniform grid of 576 special points³⁴ in the irreducible part of the SBZ and a Gaussian energy smearing scheme with a width of 0.2 eV.³⁵ Within the linear-response theory, the dynamical matrices and the e–ph matrix elements are calculated on a (12×12) grid of wave vectors in the two-dimensional irreducible SBZ. All results have been checked for convergence with respect to both the number of special points and the plane-wave energy cutoff.

The Tl(0001) surface is modeled by a supercell geometry. We used repeated slabs composed of 10 Tl layers and separated by 7.5 atomic layers of vacuum region. Atomic positions within the Tl(0001) planes maintain the symmetry of the bulk, and their lateral positions are fixed at the theoretical bulk lattice parameter, while the vertical positions of layers are relaxed until the force becomes smaller than 0.1 mRy/a.u.

III. CALCULATION RESULTS AND DISCUSSION

We used the bulk Tl lattice parameter optimized via the total-energy minimization,¹⁶ $a = 6.459$ au (without SO) and $a = 6.417$ au (with SO), as the in-plane lattice constant for the Tl(0001) slabs. The theoretical bulk values are close to the experimental parameter,³⁶ $a = 6.496$ au obtained at 5.2 K. We note that the lattice constant is weakly affected by the SO coupling,¹⁶ its inclusion produces a decrease of less than 0.7%. The calculated relaxation of Tl(0001) layers shows a very small contraction of the two outermost interlayer spacings relative to the bulk distance. The optimized geometry gives $\Delta d_{12} \approx -0.2\%$ and $\Delta d_{23} \approx -1\%$ and is also practically not affected by the SO coupling.

The surface force constants have been calculated ab initio for a 10-layer slab. Then the slab thickness was raised to 50 layers through the slab-filling procedure, i.e., the insertion of bulk layers with ab initio bulk force constants between relaxed surface layers on one side and unrelaxed surface layers on the other side. This allows one to appreciate in a single calculation the effects of the surface relaxation on the phonon dispersion curves. The surface force constants were obtained by interpolation of a (12×12) \mathbf{q} point mesh for the hexagonal SBZ, whereas the ab initio bulk force constants were obtained from a similar calculation using a $(12 \times 12 \times 4)$ \mathbf{q} point mesh. The resulting phonon dispersion curves for the 50-layer slab of Tl(0001) are shown in Figure 1. Since the slab used in the calculation was asymmetric

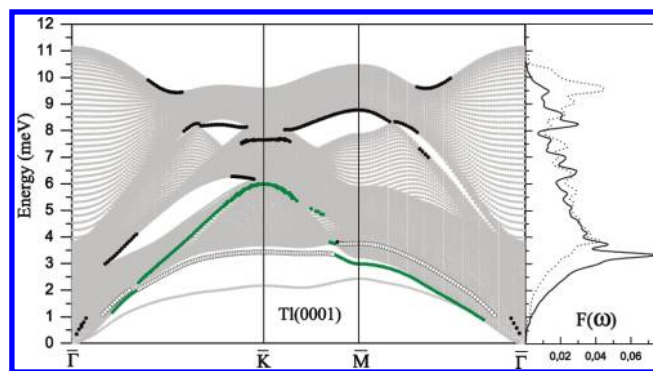


Figure 1. Phonon dispersion curves for a 50-layer Tl(0001) slab calculated with SO coupling. The phonon spectrum contains surface modes related to both relaxed (full and open circles) and ideal bulk-truncated surfaces (gray dots, the lowest phonon mode). The right panel shows the phonon DOS, $F(\omega)$, for the surface (solid line) and central (dotted line) layers of the relaxed slab.

with one relaxed surface and the other corresponding to the ideal bulk-truncated case, the phonon spectrum contains surface modes related to both types of surfaces. Surface localized phonon modes indicated by full and open circles in the figure belong to the relaxed surface, whereas the low-lying gray localized branch belongs to the unrelaxed surface. The dispersion curves of the higher surface modes for the unrelaxed surface are fairly close to the corresponding modes for the relaxed surface.

The lowest surface phonon branch for the relaxed surface in the $\Gamma\bar{K}$ direction and along most of the $\bar{K}\bar{M}$ boundary of the SBZ (Figure 1, open circles) has a quasi-shear vertical (SV) polarization and is associated with the ordinary Rayleigh wave (RW). The upper acoustic branch (green circles), showing an almost straight dispersion in both symmetry directions except near the SBZ boundary, has a quasi-shear horizontal (SH) polarization along $\Gamma\bar{K}$ and $\bar{K}\bar{M}$. After an avoided crossing near \bar{M} with the RW branch, it becomes exactly SH in the $\bar{M}\bar{\Gamma}$ direction and localized below the bulk edge, whereas the RW enters into the bulk continuum, keeping, however, its surface-localized character. The other surface branches (black circles) showing up in the gaps, above the bulk band maximum, around the \bar{K} point at 7.6 meV and near $\bar{\Gamma}$, are mostly polarized in the sagittal plane. The last one near $\bar{\Gamma}$ corresponds to the quasi-longitudinal (L) acoustic branch, which has along $\Gamma\bar{K}$ its continuation in the gap mode between 3 and 4 meV and ends at \bar{K} where it becomes degenerate with the SH surface mode. Note that at \bar{K} the SH modes are all degenerate with a L mode by symmetry, whereas the nondegenerate modes have a pure SV polarization. In the surface projected phonon density of states (DOS), $F(\omega)$ (Figure 1, right panel, full line), the largest two peaks at 3.3 and 3.7 meV clearly correspond to the flat portions of the SV branch along the SBZ boundary and near the \bar{K} point, respectively. Similarly, the gap modes of prevalent L polarization falling around 6 meV and between 8 and 9 meV contribute the remaining prominent features of $F(\omega)$. The comparison with the DOS projected onto a bulk layer at the center of the slab (Figure 1, right panel, dotted line) shows the expected shift of the spectral features to lower energies when moving to the surface.

Figure 2b shows the surface projected phonon DOS calculated for a 10-layer Tl(0001) slab with and without SO coupling. The corresponding phonon dispersion curves obtained with SO

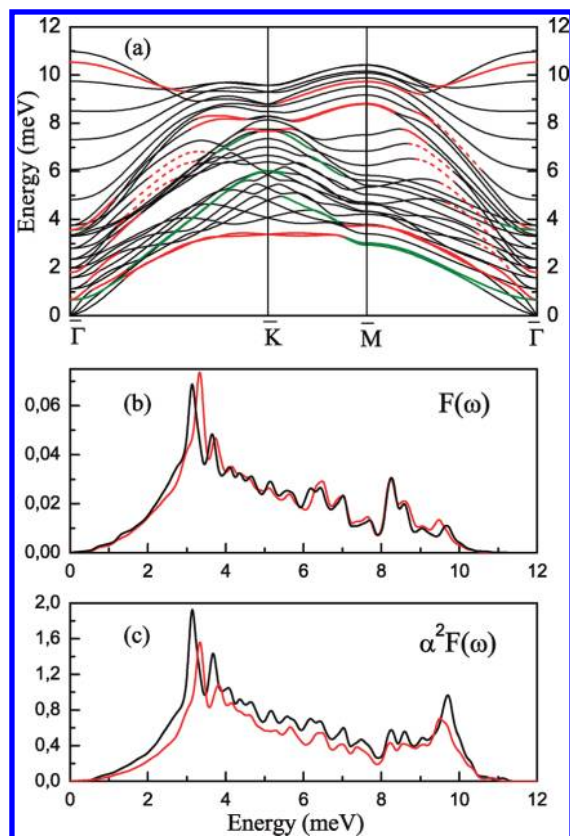


Figure 2. (a) Phonon dispersion curves for a 10-layer TI(0001) slab calculated with SO coupling. Surface localized modes and resonances (red solid and dashed lines, respectively) are mostly polarized in the sagittal plane. Surface localized modes with a shear (or quasi-shear) horizontal polarization are shown by green lines. (b) Phonon DOS, $F(\omega)$, projected onto the surface layer of a 10-layer TI(0001) slab and (c) the corresponding Eliashberg spectral function, $\alpha^2 F(\omega)$, at the Fermi energy of the TI(0001) slab with (red lines) and without (black lines) SO coupling.

coupling are shown in Figure 2a. We do not show the dispersion curves without SO coupling since on the scale of the figure the SO effects on the phonon energies are hardly visible. The SO coupling induces a modification of some phonon frequencies which, in general, is smaller than 2.5%, resulting in an almost identical phonon DOS. There is, however, a major effect of the SO coupling consisting in a stiffening of the lowest surface phonon branch, the Rayleigh mode, along the SBZ boundary. The difference in energy comes up to $\sim 7\%$ at the \bar{K} point and even more than 10% at \bar{M} . The effect can be seen in the shift of the 3.3 and 3.7 meV peaks in Figure 2b. The inclusion of the SO coupling also markedly modifies the frequencies of the highest optical modes (the 9.7 meV peak in the DOS), which soften by about 0.24 meV ($\sim 2\%$) around the SBZ center and along the $\Gamma\bar{K}$ ($[10\bar{1}0]$) direction.

We have also evaluated the strength of the e–ph interaction at the Fermi energy (E_F) of the surface:³⁷

$$\lambda_{E_F} = 2 \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega \quad (1)$$

Here $\alpha^2 F(\omega)$ is the Eliashberg spectral function, which measures the contribution of phonons with frequency ω to the e–ph

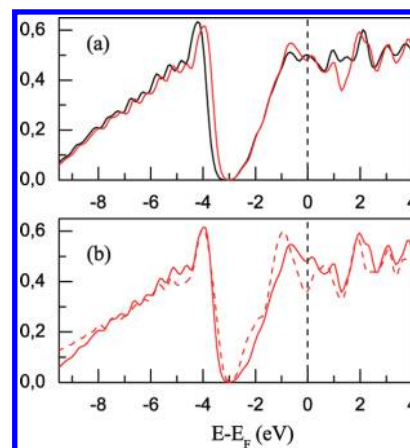


Figure 3. (a) Electronic DOS per atom for the surface layer of a 10-layer TI(0001) slab with (red line) and without (black line) SO coupling. (b) Electronic DOS with SO coupling at the surface (red solid line) and central (red dashed line) layers of a 10-layer TI(0001) slab.

coupling:³⁸

$$\alpha^2 F(\omega) = \frac{1}{N_{E_F}} \sum_{\mathbf{q}, \nu} \delta(\omega - \omega_{\mathbf{q}, \nu}) \times \sum_{\mathbf{k}, n, n'} \delta(\varepsilon_{\mathbf{k}, n} - E_F) \times |g^{n, n'}(\mathbf{k}, \mathbf{q}, \nu)|^2 \times \delta(\varepsilon_{\mathbf{k}+\mathbf{q}, n'} - E_F) \quad (2)$$

where $g^{n, n'}(\mathbf{k}, \mathbf{q}, \nu)$ is the e–ph matrix element, $\varepsilon_{\mathbf{k}, n}$ and $\varepsilon_{\mathbf{k}+\mathbf{q}, n'}$ are electronic energies, and N_{E_F} is the DOS at E_F . The summation is carried out over combinations of electronic states \mathbf{k}, n and $\mathbf{k} + \mathbf{q}, n'$ both lying at the Fermi level and phonon modes (\mathbf{q}, ν) .

The calculated e–ph coupling strength, λ_{E_F} (1.2, without SO), is a little larger than the value obtained at the Fermi surface of bulk TI, $\lambda_{E_F}^{\text{bulk}} = 0.87$ (1.0).¹⁶ An analysis of the electronic states whose contribution to the e–ph interaction is predominant revealed that these states are partly or entirely of p_z symmetry, where z is the axis normal to the surface. Like in bulk TI, the inclusion of SO coupling leads to a weakening of the coupling strength, which is reduced by about 16%. Although λ_{E_F} is proportional to the number of electronic states at the Fermi level, one cannot explain the modification of λ_{E_F} only by the corresponding change in the electronic density. Figure 3a shows the local density of the electronic states (LDOS) for the surface TI(0001) layer calculated both with (red line) and without SO coupling (black line). Similarly to the case of bulk TI,¹⁶ the SO coupling produces only minor modifications. There is a small shift (~ 0.2 eV) of the electronic states, which are mainly s -like in character, toward the bands near the Fermi level. The latter, which are predominantly p -like in character,^{39,40} exhibit an enhancement of LDOS in the region from 1.0 to 0.2 eV below the Fermi energy due to the SO-induced increase of the binding energy. With respect to the DOS at E_F , it is decreased by only 8% (from 0.229 to 0.212 states/(eV atom)) due to the SO effects. Thus, the change in the number of electronic states at E_F available for scattering processes accounts for roughly half of the decrease of λ_{E_F} .

It is important to note that there are no well-pronounced surface electronic states in the energy gaps. The states with preferable localization near the surface lie inside the bulk-like electronic bands and have a resonant character. In Figure 3b we compare the LDOS for the surface and central layers of the TI(0001) slab.

Perturbations caused by the surface do not penetrate far into the bulk and affect only two upper layers. One of the surface manifestations is an enhancement of the LDOS's for the surface and subsurface atoms around the Fermi energy. They become $\sim 35\%$ and $\sim 20\%$ larger, respectively, as compared to the LDOS for the central layer atoms. This is largely a consequence of numerous surface resonances existing in the energy region.

The phonon frequencies are one more factor that essentially determines the value of λ_{E_F} . The effect of SO coupling on the Eliashberg spectral function is shown in Figure 2c. On the one hand, it results in a shift of the low-energy peak to higher frequencies due to the stiffening of the lowest-lying surface phonon modes. On the other hand, the inclusion of the SO coupling modulates the heights of the $\alpha^2F(\omega)$ peaks. Both processes promote a decrease of λ_{E_F} .

IV. SUMMARY

We have presented an analysis based on ab initio calculations of the influence of the SO interaction on the phonon spectrum of the Tl(0001) surface. We find that, in general, the effect of the SO coupling on both the optimized geometry and the lattice dynamics of the Tl(0001) surface is weak. The calculated relaxation of Tl(0001) layers is small and practically not affected by the SO coupling too. The SO-induced modifications of the calculated phonon frequencies are smaller than 2.5% except for the Rayleigh mode at the SBZ boundar, which stiffens by 7–10%. We have also evaluated the e–ph interaction at the Fermi level of the surface with and without SO effects. We find that the e–ph coupling strength λ_{E_F} is reduced by 16% when the SO interaction is taken into account. Both the change in the number of electronic states at E_F available for scattering processes and the modification of the phonon spectrum, especially the stiffening of the lower-energy surface phonon modes, account for the decrease of the e–ph coupling strength.

AUTHOR INFORMATION

Corresponding Author

*E-mail: waptctce@sq.ehu.es.

ACKNOWLEDGMENT

We acknowledge financial support from the University of the Basque Country, the Departamento de Educación del Gobierno Vasco (IT-366-07), and the Spanish Ministerio de Ciencia e Innovación (Grant No. FIS 2010-19609-C02-01). G.B. acknowledges the support of Ikerbasque under the project ABSIDES.

REFERENCES

- (1) Koroteev, Yu. M.; Bihlmayer, G.; Chulkov, E. V.; Blügel, S. *Phys. Rev. B* **2008**, *77*, 045428.
- (2) Ast, C. R.; Henk, J.; Ernst, A.; Moreschini, L.; Falub, M. C.; Pacil, D.; Bruno, P.; Kern, K.; Grioni, M. *Phys. Rev. Lett.* **2007**, *98*, 186807.
- (3) Bihlmayer, G.; Blügel, S.; Chulkov, E. V. *Phys. Rev. B* **2007**, *75*, 195414.
- (4) Dil, J. H. *J. Phys.: Condens. Matter* **2009**, *21*, 403001.
- (5) Hirahara, T.; Nagao, T.; Matsuda, I.; Bihlmayer, G.; Chulkov, E. V.; Koroteev, Yu. M.; Echenique, P. M.; Saito, M.; Hasegawa, S. *Phys. Rev. Lett.* **2006**, *97*, 146803.
- (6) Shikina, A. M.; Varykhalov, A.; Prudnikova, G. V.; Usachov, D.; Adamchuk, V. K.; Yamada, Y.; Riley, J. D.; Rader, O. *Phys. Rev. Lett.* **2008**, *100*, 057601.

- (7) Reinert, F. *J. Phys.: Condens. Matter* **2003**, *15*, S693.
- (8) Pascual, J. I.; Bihlmayer, G.; Koroteev, Yu. M.; Rust, H.-P.; Ceballos, G.; Hansmann, M.; Horn, K.; Chulkov, E. V.; Blügel, S.; Yu, M.; Echenique, P. M.; Hofmann, Ph. *Phys. Rev. Lett.* **2004**, *93*, 196802.
- (9) Hofmann, Ph.; Gayone, J. E.; Bihlmayer, G.; Koroteev, Yu. M.; Chulkov, E. V. *Phys. Rev. B* **2005**, *71*, 195413.
- (10) Hofmann, Ph. *Prog. Surf. Sci.* **2006**, *81*, 191.
- (11) Nechaev, I. A.; Jensen, M. F.; Rienks, E. D. L.; Silkin, V. M.; Echenique, P. M.; Chulkov, E. V.; Hofmann, Ph. *Phys. Rev. B* **2009**, *80*, 113402.
- (12) Gonze, X.; Michenaud, J. P. *Phys. Rev. B* **1990**, *17*, 11827.
- (13) Dal Corso, A. *J. Phys.: Condens. Matter* **2008**, *20*, 445202.
- (14) Daz-Sánchez, L. E.; Romero, A. H.; Gonze, X. *Phys. Rev. B* **2007**, *76*, 104302.
- (15) Verstraete, M. J.; Torrent, M.; Jollet, F.; Zérah, G.; Gonze, X. *Phys. Rev. B* **2008**, *78*, 045119.
- (16) Heid, R.; Bohnen, K.-P.; Sklyadneva, I. Yu.; Chulkov, E. V. *Phys. Rev. B* **2010**, *81*, 174527.
- (17) Gayone, J. E.; Hoffmann, S. V.; Li, Z.; Hofmann, Ph. *Phys. Rev. Lett.* **2003**, *91*, 127601.
- (18) Eiguren, A.; Hellsing, B.; Chulkov, E. V.; Echenique, P. M. *Phys. Rev. B* **2003**, *67*, 235423.
- (19) Sklyadneva, I. Yu.; Chulkov, E. V.; Echenique, P. M. *J. Phys.: Condens. Matter* **2008**, *20*, 165203.
- (20) Hofmann, Ph.; Sklyadneva, I. Yu.; Rienks, E. D. L.; Chulkov, E. V. *New J. Phys.* **2009**, *11*, 125005.
- (21) Nriagu, J. O. *Chem. Eng. News* **2003**, *81*, 153.
- (22) Castellarin-Cudia, C.; Surnev, S.; Ramsey, M. G.; Netzer, F. P. *Surf. Sci.* **2001**, *491*, 29–38.
- (23) Lee, S. S.; Song, H. J.; Kim, N. D.; Chung, J. W.; Kong, K.; Ahn, D.; Yi, H.; Yu, B. D.; Tochiwara, H. *Phys. Rev. B* **2002**, *66*, 233312.
- (24) Kotlyar, V. G.; Saranin, A. A.; Zotov, A. V.; Kasyanova, T. V. *Surf. Sci.* **2003**, *543*, L663–L667.
- (25) Sakamoto, K.; Eriksson, P. E. J.; Ueno, N.; Uhrberg, R. I. G. *Surf. Sci.* **2007**, *601*, S258–S261.
- (26) Hatta, S.; Aruga, T.; Kato, C.; Takahashi, S.; Okuyama, H.; Harasawa, A.; Okuda, T.; Kinoshita, T. *Phys. Rev. B* **77**, 77, 245436.
- (27) Worlton, T. G.; Schmunk, R. E. *Phys. Rev. B* **1971**, *3*, 4115–4123.
- (28) Zein, N. E. *Soviet Physics of Solid State* **1984**, *26*, 3028–3034.
- (29) Baroni, S.; de Gironcoli, S.; Dal Corso, A.; Giannozzi, P. *Rev. Mod. Phys.* **2001**, *73*, S15–S62.
- (30) Louie, S. G.; Ho, K.-M.; Cohen, M. L. *Phys. Rev. B* **1979**, *19*, 1774–1782.
- (31) Meyer, B.; Elsässer, C.; Fähnle, M. *FORTTRAN90, a program for mixed-basis calculations for crystals* (Max-Planck-Institut für Metallforschung, Stuttgart).
- (32) Vanderbilt, D. *Phys. Rev. B* **1985**, *32*, 8412–8415.
- (33) Hedin, L.; Lundqvist, B. I. *J. Phys. C* **1971**, *4*, 2064–2083.
- (34) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188–5192.
- (35) Ho, K. M.; Fu, C. L.; Harmon, B. N. *Phys. Rev. B* **1984**, *29*, 1575–1587.
- (36) Barrett, C. S. *Phys. Rev.* **1958**, *110*, 1071–1072.
- (37) Allen, P. B.; Cohen, M. L. *1969 Phys. Rev.* **1969**, *187*, 525–538.
- (38) *Selected Topics in Solid State Physics*; Grimvall, G. 1981 The Electron–Phonon Interaction in Metals Eds.; Wohlfarth, E.: New York: North-Holland, 1981.
- (39) Ament, M. A. E. A.; de Vroomen, A. R. *J. Phys. F: Metal Phys.* **1977**, *7*, 97–104.
- (40) Holtham, P. M.; Jan, J.-P.; Skriver, H. L. *J. Phys. F: Metal Phys.* **1977**, *7*, 635–646.