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Surface core-level shifts in $\mathrm{CdTe}_{1-x}\mathrm{S}_x(110)$ and $\mathrm{CdTe}_{1-x}\mathrm{Se}_x(110)$

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The metal chalcogenides $\mathrm{CdTe}_{1-x}\mathrm{S}_x$ and $\mathrm{CdTe}_{1-x}\mathrm{Se}_x$ for $x=0.05$ have been studied with core-level spectroscopy. It was found that the surface core-level shifts of the Cd 4*d* and Te 4*d* spectra of these ternary compounds were quite small and similar to those of the binary compound CdTe. However, the S 2*p* and also the Se 3*d* spectra of the first surface layer showed much larger energy shifts toward lower binding energies than tellurium. The results are discussed in terms of initial- and final-state effects describing the x-ray photoemission process.

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I. INTRODUCTION

During the previous years, there has been a great interest in cadmium chalcogenides.[1–5] These semiconductors have been used, for instance, to investigate electrical properties of grain boundaries and crystal growth from vapor. In particular, CdTe is a promising material in solar cells and in other optoelectronic devices[6,7] as well as in infrared, x-ray, and γ-ray detectors. Nanocrystals of CdTe, CdS, and CdSe have been studied for their photoluminescence properties as a function of their particle size.[8,9] Recently, it has been found that adding 1-decanethiol to CdTe nanoparticles can result in a $\mathrm{CdTe}_{1-x}(\mathrm{SC}_{10})_x$ shell at the surface having the particle size unchanged although the concentration of tellurium is now smaller.[10] When the Te concentration decreases, the emitting light will be blueshifted. In spite of these findings not so much is known about the $\mathrm{CdTe}_{1-x}\mathrm{S}_x(110)$ and $\mathrm{CdTe}_{1-x}\mathrm{Se}_x(110)$ surfaces.

Nowadays, the binding energy of the core levels can be measured with high accuracy. The photoelectron spectroscopy is used to study the binding energy difference of the surface layer spectra relative to the bulk layer ones. This appears as a surface core-level shift (SCLS) that is characteristic for each compound and also for the elements. The photon energy can be changed in such a way that the measurements are more surface sensitive, which enables the observation of small shifts in binding energy. Depending on the work function of the instrument, the most surface-sensitive measurement will be achieved when the photon energy is about 50–60 eV larger than the binding energy of the specific core-level spectrum. A higher excitation energy means that a bigger part of the signal comes from the bulk.

The (110) surface of CdTe has received considerable attention.[3] Also, the (100) orientation of Cd(Zn)Te has to be mentioned.[5] In this study we mainly concentrate on the S 2*p* and Se 3*d* core-level spectra of $\mathrm{CdTe}_{1-x}\mathrm{S}_x$ and $\mathrm{CdTe}_{1-x}\mathrm{Se}_x$ with $x=0.05$. Having the same crystal structure, these compounds are useful for studies of the screening process in photoemission. For many semiconducting compounds the ground-state properties of the electronic structure have been able to explain their surface core-level shifts.[11] However, it has been shown that for silicon and germanium the final-state effect gives an important contribution.[12] Therefore, it is necessary to be able to separate these phenomena. Usually, this has been done by performing a density functional calculation for the SCLS.[12] It is also of interest to discuss how the final state of the x-ray photoemission spectroscopy (XPS) process affect the experimental results.

II. EXPERIMENT

Single crystals of the ternary compounds $\mathrm{CdTe}_{1-x}\mathrm{S}_x$ and $\mathrm{CdTe}_{1-x}\mathrm{Se}_x$ were made using the self-selecting vapor growth method.[7] They were grown in almost isothermal ampoules; thus the solid solutions are uniform. The uniformity was confirmed by lattice constant studies. The measured values varied in quite a small range, whatever the reference data. The nominal composition of sulfur and selenium was $x=0.05$. Standard XPS measurements of the samples gave about 2 at. % for both S and Se, which is slightly lower than the expected value of 2.5 at. %. No impurities were detected in the spectra of the cleaved surfaces. Below the solubility limit, the crystal structure of these solid solutions is cubic zinc blende[13–15] (for $\mathrm{CdTe}_{1-x}\mathrm{Se}_x$ the solubility limit is $x<0.2$).

The measurements were carried out at the MAX II synchrotron laboratory in Lund, Sweden. Beamline I411 was equipped with an SX-700 PGM monochromator and Scienta SES-200 analyzer. The energy resolution of the instrument was estimated to be better than 40 meV for our spectra. The Au 4*f* doublet and the Fermi level were used to calibrate the binding energy scale. The fresh (110) surfaces of vapor-grown crystals of $\mathrm{CdTe}_{1-x}\mathrm{S}_x$ and $\mathrm{CdTe}_{1-x}\mathrm{Se}_x$ were made by cleaving in ultrahigh vacuum at room temperature. The low-energy electron diffraction (LEED) of the compounds was also considered. The (1×1) LEED patterns of an ordered (110) zinc blende surface were clear and sharp.[16–18]

The spectra were measured using the following excitation energies: S 2*p* with 210, 225, 250, and 350 eV, Se 3*d* with 125, 150, and 250 eV, Te 4*d* with 100 and 210 eV, and Cd

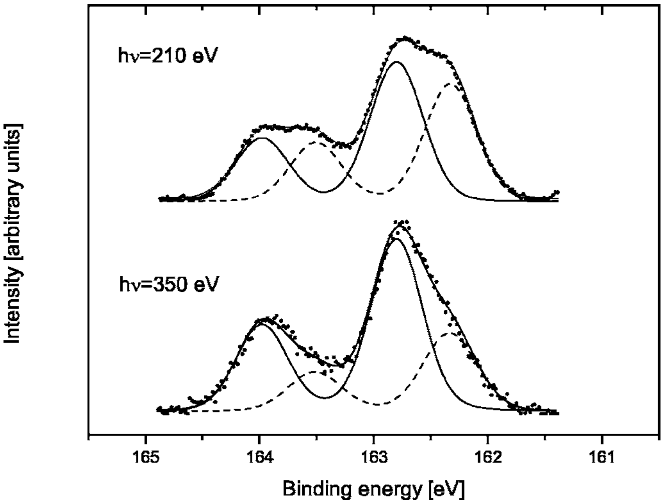

FIG. 1. The S 2*p* spectra of $CdTe_{1-x}S_x$ with $x=0.05$ measured with excitation energies of 210 eV (upper spectrum) and 350 eV. The solid line denotes the bulk component and the dashed one describes the surface one.

TABLE I. The surface core-level shifts of the S 2*p*, Cd 4*d*, and Te 4*d* signals of the $CdTe_{1-x}S_x$ compound with different photon energies.

	Excitation energy (eV)	SCLS (eV)
S 2*p*	210	−0.47±0.02
S 2*p*	225	−0.46±0.02
S 2*p*	250	−0.47±0.02
S 2*p*	350	−0.47±0.02
Cd 4*d*	70	+0.27±0.02
Cd 4*d*	210	+0.27±0.02
Te 4*d*	100	−0.26±0.02
Te 4*d*	210	−0.24±0.02

4*d* with 70 and 210 eV. The valence band was recorded with a photon energy of 70 eV. After background subtraction the spectra were fitted with true Voigt line shapes. For the S 2*p* and Se 3*d* peaks the full width at half maximum of the Lorentzian was about 0.07 eV and the Gaussian about 0.3 eV. The latter, for some spectra, varied within 0.1 eV due to the difference of the excitation energy and the phonon broadening of the core levels.

III. RESULTS AND DISCUSSION

Different excitation energies were used to measure the S 2*p* and Se 3*d* spectra to investigate the relative intensity of the surface signal. These spectra were then fitted using convoluted Gaussian-Lorentzian line shapes as can be seen from Figs. 1 and 2. A monotonic decrease of the surface peak intensity relative to that of the bulk peak is observed when the photon energy is increased. The surface components are shifted toward lower binding energies. The SCLS for the S 2*p* spectrum is about −0.47 eV and for Se 3*d* it is −0.35 eV. It is interesting to note that the corresponding shift of the Te 4*d* spectrum is about −0.26 eV in $CdTe_{1-x}S_x$ (Table I) and in $CdTe_{1-x}Se_x$ the value is only slightly smaller, being −0.24 eV (Table II and Fig. 3). For pure CdTe the Te 4*d* SCLS has been observed to be very similar; for instance, Prince *et al.*[3] obtained −0.26±0.05 eV for this line. In this case a nonlocal screening, largely caused by *s* and *p* electrons, can be assumed.[19]

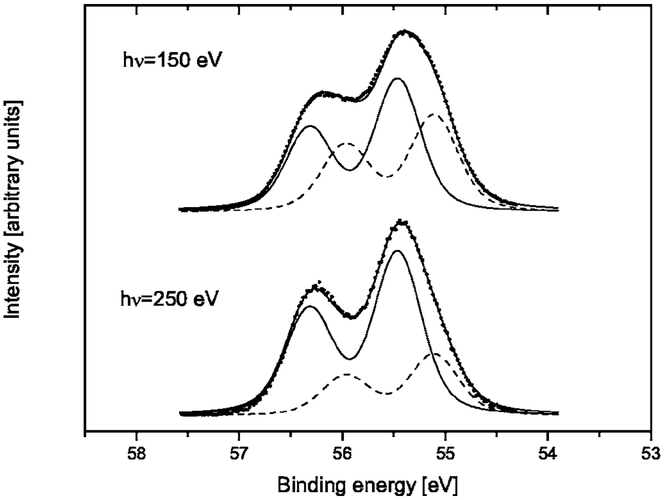

FIG. 2. The Se 3*d* spectra of $CdTe_{1-x}Se_x$ having $x=0.05$ measured with photon energies of 150 and 250 eV.

The Cd 4*d* doublet has been assumed to be slightly distorted by the Te 5*s* signal,[3,20] which can be seen on the low-binding-energy side of the bulk feature in Fig. 4. Also, the S 3*s* and Se 4*s* bands are in this energy region,[21] although their contribution to the tail of the spectrum should be even smaller. However, the core-level spectra in crystalline solids are caused by fully occupied bands. These bands are much narrower in energy on going to deeper binding energies compared with those of shallow ones. In the CdSe(110) and CdTe(110) surfaces a considerable dispersion has been observed for the Cd 4*d* band.[22] This effect has been interpreted to be the main reason for the low-energy shoulder, especially when the photon energy is about 70 eV.[22] The appearance of this feature is also supported by a band structure calculation.[23]

The XPS valence bands of the ternary compounds and the total density of states of CdTe calculated by Wei and Zunger can be seen in Fig. 5. The features below the valence band

TABLE II. The SCLSs of the Se 3*d*, Cd 4*d*, and Te 4*d* spectra of the $CdTe_{1-x}Se_x$ compound.

	Excitation energy (eV)	SCLS (eV)
Se 3*d*	125	−0.35±0.02
Se 3*d*	150	−0.35±0.02
Se 3*d*	250	−0.35±0.02
Cd 4*d*	70	+0.26±0.02
Cd 4*d*	210	+0.26±0.02
Te 4*d*	100	−0.23±0.02
Te 4*d*	210	−0.24±0.02

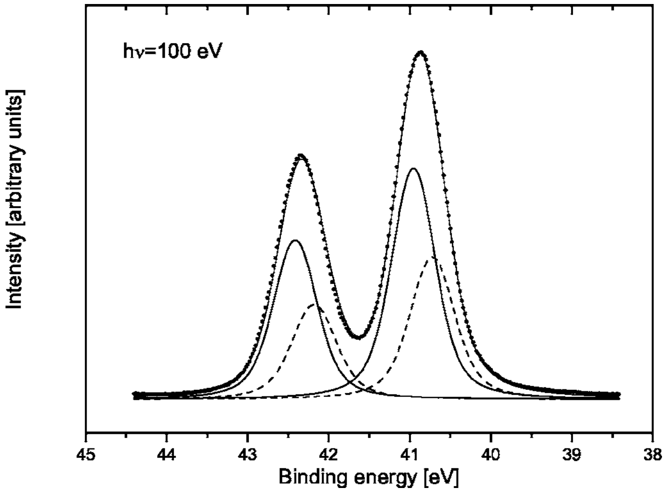

FIG. 3. The Te 4*d* spectrum of $\mathrm{CdTe}_{1-x}\mathrm{Se}_x$ for $x=0.05$ measured with an excitation energy of 100 eV.

maximum down to 3 eV in binding energy can be largely ascribed to the Te 5*p* states.[21] The strong peak having a binding energy of 4 eV is due to the Te 5*p*– and Cd 5*s*–like states. However, this latter structure is more intense for $\mathrm{CdTe}_{1-x}\mathrm{Se}_x$ than for $\mathrm{CdTe}_{1-x}\mathrm{S}_x$. This kind of behaviour is similar to those of ZnSe and ZnS,[24] the contribution of Se 4*p* being stronger than that of S 3*p* in this energy region.

On the basis of the discussion above one can explain the nonlocal screening of the Cd 4*d* core hole to be largely caused by the Te 5*p*–like electrons near the valence band maximum. Regarding the anion in the compound, one can anticipate that the screening should be more efficient in the case of pure Te than in CdTe.

As a cation, Cd has a positive surface core-level shift of +0.26 eV for the 4*d* peak, indicating that the surface component has been shifted to higher binding energies relative to that of the corresponding bulk feature. One should also mention that Prince *et al.*[3] have obtained a shift of +0.24 for the Cd 4*d* line in CdTe(110), which is quite close to our result. Also, Wall *et al.*[4] have reported a value of +0.22±0.03 eV for the same line. The density of states is rather localized in energy for S and Se causing a hybridization with the CdTe valence bands. Therefore, it seems that this hybridization effect does not give any strong contribution to the SCLSs of the Cd 4*d* and Te 4*d* lines. On the other hand, for the CdTe(100) (Ref. 2) and Cd(Zn)Te(100) (Ref. 5) surfaces much larger SCLSs for Cd have been measured, about +0.6 and +0.7 eV, respectively, emphasizing the role of the surface orientation of the specimen.

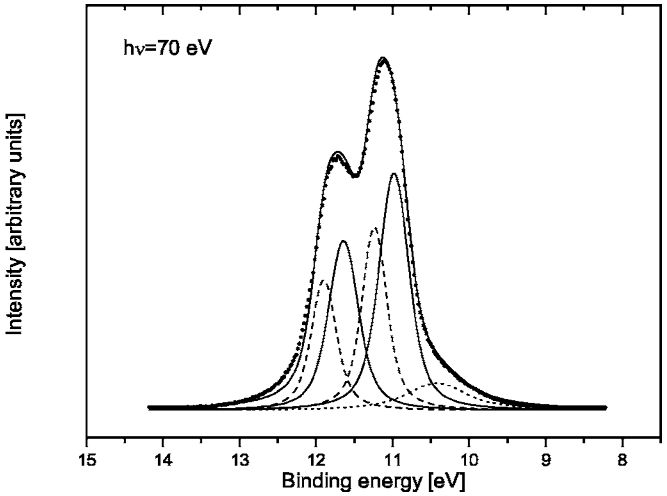

FIG. 4. The Cd 4*d* doublet of $\mathrm{CdTe}_{1-x}\mathrm{Se}_x$ for $x=0.05$ measured with an excitation energy of 70 eV. The small component described by a dotted line on the low-binding-energy side of the spectrum is discussed in the text.

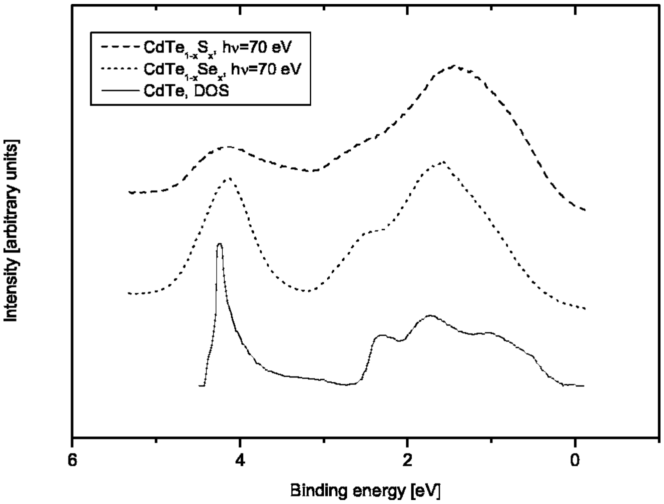

FIG. 5. The XPS valence bands of $\mathrm{CdTe}_{1-x}\mathrm{S}_x$ (dashed line) and $\mathrm{CdTe}_{1-x}\mathrm{Se}_x$ (dotted line) and the total density of states of CdTe (solid line).

The anions S, Se, and Te belong to Group VIA in the Periodic Table. Furthermore, they all have Cd atoms as nearest neighbors, which means that their environment is very similar in the case of our compounds. Usually, the surface core-level shift, especially for metals, has been regarded as an effect that arises from the reduction of the coordination number of the surface atom in comparison with the bulk one.[15] This is a typical initial-state phenomenon and it gives a strong contribution to the so-called chemical shift.[25] On the basis of the arguments above one could expect that the initial-state effect on the SCLS would be very similar for all the anions since the coordination numbers are the same and the nearest neighbors are cations. Of course, there will also be some changes in electronic charge redistributions around the different surface anions largely due to hybridization effects around these atoms, but we do not expect that these would be significant, since the local electronic density of states should be rather narrow in energy for S and Se of the compounds due to the small concentration of these atoms. This can be explained with the rigid band approximation,[26,27] which means that the core-level shift of the element has the same behavior as that of the center of gravity for the valence band. When the local valence band is narrow in energy the hybridization effect gives a very small contribution to the energy position of the center of gravity. On the other hand this argument does not hold for Te which has a more delocalized valence band.[20] Nevertheless, the reduction of the

SCLS is still systematic regarding the increase of the atomic number of the anion.

GaAs is more covalent than CdTe having the same crystal structure. In terms of the surface Madelung potential, the most significant factor between these compounds is the change of the bulk charge transfer arising from the differencies in ionicities. Since the lattice parameters do not deviate much from each other, the theoretical initial-state SCLSs due to the Madelung potential should be about two times larger for CdTe than for GaAs. Hence, the calculated[3] value for Cd should be about −0.70 eV and for Te it would be about 0.53 eV, not in agreement with experiment. Regarding the ternary compounds, the electronegativity of the element Te is larger than those of S and Se, whereas the corresponding values are very similar for the latter. Therefore, one would expect that the SCLSs for S and Se should be similar, but as can be seen from Tables I and II this is not the case. Using charge transfer arguments, it is hard to explain the shifts as being caused by initial-state effects.

As pointed out by Davenport *et al.*[28] the smaller coordination number of the surface atom not only affects the surface Madelung potential in the initial state of the XPS process, giving the opposite SCLS to the cation and the anion with the same absolute energy value, but also makes the screening of the core hole less pronounced in comparison with that of the corresponding bulk ionization in the final state. This final-state effect would reduce the SCLS for the anion, giving a larger binding energy in the case of the surface component of the spectrum. Provided the effect of the final-state screening is the same for the surface atom and the bulk one, good agreement between experiments and initial-state tight-binding calculations, assuming charge neutrality of the surface layers, can be expected for semiconducting binary compounds.[11,29] However, the changes in the Madelung potential are not always able to explain the binding energy differences between the XPS spectra of atoms.[3,28] The possible relaxation and reconstruction of the surface layer can also[18] affect slightly the binding energy of the corresponding cation or anion peak.[8,30] For instance, in the case of the CdTe(110) surface the topmost anions have been estimated to be moved upward about 0.18 Å and the cations downward about 0.64 Å.[18] However, in our case the SCLS of S, Se, and Te decreases as the atomic number increases. This can be explained to be due to a less complete final-state screening of the core hole in the surface atom relative to that of the bulk atom for a heavier anion[31] causing a shift of the surface peak to higher binding energies.[32] For Cd the final-state screening in the surface cation is increased, causing a shift to lower binding energies. Only in the case when screening of the core-ionized surface atom differs from that of the corresponding bulk atom can the final-state contribution to the SCLS be observed.

As a conclusion one can note that the screening of the core hole of S and Se atoms in the bulk of the compounds is already rather strong. The final-state effect in these anions is not expected to be so significant as in the pure CdTe compound in reducing the SCLS, since for the Te core-level spectrum the binding energy difference between the surface and the bulk peak is smaller than for those of sulfur and selenide.

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[1] M. Taniguchi, L. Ley, R. L. Johnson, J. Ghijsen, and M. Cardona, Phys. Rev. B **33**, 1206 (1986).
[2] P. John, T. Miller, T. C. Hsieh, A.P. Shapiro, A. L. Wachs, and T. C. Chiang, Phys. Rev. B **34**, 6704 (1986).
[3] K. C. Prince, G. Paolucci, V. Chab, M. Surman, and A. M. Bradshaw, Surf. Sci. **206**, L871 (1988).
[4] A. Wall, Y. Gao, A. Raisanen, A. Franciosi, and J. R. Chelikowsky, Phys. Rev. B **43**, 4988 (1991).
[5] C. Heske, U. Winkler, G. Held, R. Fink, E. Umbach, Ch. Jung, P. R. Bressler, and Ch. Hellwig, Phys. Rev. B **56**, 2070 (1997).
[6] A. Ennaoui, S. Fiechter, Ch. Pettenkofer, N. Alonso-Vante, K. Büker, M. Bronold, Ch. Hüpfner, and H. Tributsch, Sol. Energy Mater. Sol. Cells **29**, 289 (1993).
[7] K. Durose, A. Yates, A. Szczerbakow, J. Domagala, Z. Golacki, and K. Swiatek, J. Phys. D **35**, 1997 (2002).
[8] X. Wang, W. W. Yu, J. Zhang, J. Aldana, X. Peng, and M. Xiao, Phys. Rev. B **68**, 125318 (2003).
[9] H. Borchert, D. V. Talapin, N. Gaponik, C. McGinley, S. Adam, A. Lobo, T. Möller, and H. Weller, J. Phys. Chem. B **107**, 9662 (2003).
[10] K. Akamatsu, T. Tsuruoka, and H. Nawafune, J. Am. Chem. Soc. **127**, 1634 (2005).
[11] C. Priester, G. Allan, and M. Lannoo, J. Vac. Sci. Technol. B **11**, 1638 (1993).
[12] E. Pehlke and M. Scheffler, Phys. Rev. Lett. **71**, 2338 (1993).
[13] K. Ohata, J. Saraie, and T. Tanaka, J. Appl. Phys. **12**, 1198 (1973).
[14] K. Ohata, J. Saraie, and T. Tanaka, J. Appl. Phys. **12**, 1641 (1973).
[15] G. Allan, Phys. Rev. B **43**, 9594 (1991).
[16] J. Fritsche, A. Thissen, A. Klein, and W. Jaegermann, Thin Solid Films **387**, 158 (2001).
[17] K. Yong, A. J. Gellman, and P. J. Sides, Surf. Sci. **374**, 65 (1997).
[18] C. B. Duke, A. Paton, W. K. Ford, A. Kahn, and G. Scott, Phys. Rev. B **24**, 3310 (1981).
[19] C. Calareso, V. Grasso, and L. Silipigni, Appl. Surf. Sci. **171**, 306 (2001).
[20] S. H. Wei and A. Zunger, Phys. Rev. B **35**, 2340 (1987).
[21] S. Wiklund, K. O. Magnusson, and S. A. Flodström, Surf. Sci. **238**, 187 (1990).
[22] K. O. Magnusson, G. Neuhold, K. Horn, and D. A. Evans, Phys. Rev. B **57**, 8945 (1998).
[23] D. Vogel, P. Kruger, and J. Pollmann, Phys. Rev. B **54**, 5495 (1996).
[24] R. Laihia, J. A. Leiro, K. Kokko, and K. Mansikka, J. Phys.:

Condens. Matter **8**, 6791 (1996).

[25] P. S. Bagus, C. R. Brundle, G. Pacchioni, and F. Parmigiani, Surf. Sci. Rep. **19**, 265 (1993).

[26] P. H. Citrin and G. K. Wertheim, Phys. Rev. B **27**, 3176 (1983).

[27] F. M. Alamgir, H. Jain, A. C. Miller, D. B. Williams, and R. B. Schwarz, Philos. Mag. B **79**, 239 (1999).

[28] J. W. Davenport, R. E. Watson, M. L. Perlman, and T. K. Sham, Solid State Commun. **40**, 999 (1981).

[29] T. Kendelewicz, P. H. Mahowald, K. A. Bertness, C. E. McCants, I. Lindau, and W. E. Spicer, Phys. Rev. B **36**, 6543 (1987).

[30] I. G. Batyrev, L. Kleinman, and J. Leiro, Phys. Rev. B **70**, 073310 (2004).

[31] M. Methfessel, D. Hennig, and M. Scheffler, Surf. Sci. **287/288**, 785 (1993).

[32] T. Miller, E. Rosenwinkel, and T. C. Chiang, Solid State Commun. **47**, 935 (1983).