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Element-specific gap in the p states for ternary semiconductors CuGaSe₂ and ZnGeAs₂ via alignment of x-ray emission and x-ray absorption spectra

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Abstract

X-ray emission and x-ray absorption spectra at the K-edges of ternary semiconductors CuGaSe₂ and ZnGeAs₂ are aligned by measuring the corresponding $K\beta_{1,3}$ line in the apparatus used for recording the emission spectra and in the apparatus used for recording the absorption spectra.

This makes it possible to determine the *element-specific* x-ray gap in the p states and to observe that this gap decreases if the electronegativity of the corresponding element increases.

Additionally, spectra related to different atoms of the same compound were aligned by relying on theoretical x-ray emission bands. Calculations based on the local density approximation are able to reproduce the mutual positions of x-ray absorption bands of different elements of the same compound provided that a universal correction for the predicted onset of the conduction band is applied (by means of the so-called scissors operator).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Ternary semiconductors of the I–III–VI₂ and II–IV–V₂ types with chalcopyrite structure have been studied extensively in the past. From a fundamental physics point of view, they offer an opportunity to study systematic variations of their properties with chemical composition. From an applications point of view, they are promising materials for photovoltaics and electrochemistry. Understanding the electronic structure of materials is often a necessary prerequisite for their broader use. Among the techniques which probe the electronic states, x-ray absorption and x-ray emission spectroscopies hold unique positions because they offer a local angular-momentum-selected view of the occupied and unoccupied states from a chemically specific site.

Experimental and theoretical x-ray emission spectra (XES) at the K-edges of CuGaSe₂ and ZnGeAs₂ (involving transitions from the p symmetry valence states to the 1s core states) were published in [1]. Experimental and theoretical

x-ray absorption spectra (XAS) at the K-edges of these compounds (involving transitions from the 1s core states to the p symmetry unoccupied states) were published in [2]. Good agreement between experiment and theory was quoted in both works. However, in the case of x-ray absorption spectra, only the *shapes* of the spectral curves could have been compared—not the mutual positions of the x-ray absorption bands assigned to different elements of the compound. A more complete picture of the electronic states would be obtained if the x-ray emission and x-ray absorption spectra were mutually aligned.

In this work, we align x-ray emission and x-ray absorption spectra for the same element by measuring the corresponding $K\beta_{1,3}$ line in the apparatus used for recording XES *and* in the apparatus used for recording XAS. We can see substantial changes in the width of the forbidden x-ray gap in the p states of the compound for each of the constituent elements separately. We show that these element-specific gaps exhibit systematic trends that are similar for both ternary

semiconductors. Additionally, we align x-ray absorption spectra at the K-edges of different elements of the same compound by relying on XES, thus facilitating comparison of the positions of x-ray absorption bands as obtained by theory and by experiment.

2. Methodological framework

2.1. Experiment

The x-ray emission and absorption bands of CuGaSe₂ and ZnGeAs₂ were published in [1, 2], where the whole procedure is described in detail. Here we only summarize that the x-ray emission and x-ray absorption spectra of polycrystalline samples were measured using a two-crystal spectrometer [3, 4] and an x-ray tube. A fluorescence method was used for recording the x-ray emission spectra while the x-ray absorption spectra were obtained in the transmission mode.

2.2. Alignment of the measured x-ray emission and x-ray absorption spectra

The alignment of energy scales of the x-ray emission and x-ray absorption spectra was done via calibration measurements of the K $\beta_{1,3}$ line at both spectrometers for all the elements which constitute the investigated compound. In order to get higher intensities, the calibration measurements were performed for the following compounds: CuO, Ga₂O₃, amorphous Se, ZnO, GeO₂ and As₂S₃. For measurements on the absorption spectrometer, each compound was mixed as a powder with polystyrene and compressed to form a thin platelet.

Before the positions of the K $\beta_{1,3}$ lines measured in the emission and in the absorption spectrometer can be properly aligned, one has to correct for the different smearing of these lines in the spectrometers. Namely, because of the differences in the pairs of crystals used in the two-crystal spectrometers, in the distances between the analysing crystals and in the heights of the horizontal slits, the apparatus smearing functions of the K $\beta_{1,3}$ lines in both spectrometers differ [3, 4]. Because all measurements were performed with two-crystal spectrometers using nearly perfect Si and Ge crystals, respectively, it was possible to calculate the apparatus smearing function accurately enough. Hence our approach might be to deconvolute the measured lines, thus obtaining the K $\beta_{1,3}$ lines free from experimental distortion [5, 6]. Indeed, such a procedure was possible for the calibration measurements done by the emission spectrometer: the recorded intensity was high, meaning that the spectra were measured with a sufficient accuracy thus enabling a deconvolution. After the deconvolution, the spectral curves did not display any deformations and could be thus viewed as undistorted K $\beta_{1,3}$ lines.

On the other hand, such a procedure was not possible for the absorption spectrometer. In this case, the thin platelet of the relevant calibration compound was placed just behind the window of the x-ray tube and, consequently, the K $\beta_{1,3}$ line was excited by the continuous radiation partly absorbed in the platelet. Hence the K $\beta_{1,3}$ line was superimposed

on the continuous spectrum of the x-ray tube, yielding an intensity of the K $\beta_{1,3}$ lines essentially smaller than in the case of the emission spectrometer. Consequently, because of the relatively large scatter of the measured points, reconstruction of the undistorted K $\beta_{1,3}$ line cannot be achieved via a deconvolution. Therefore, we followed a different route to obtain the positions of undistorted calibration lines for absorption spectrometer: The undistorted K $\beta_{1,3}$ lines obtained by means of the emission spectrometer were convoluted by the smearing function of the absorption spectrometer and matched to the lines measured by means of the absorption spectrometer. This is shown in figure 1; the smearing functions are also presented to give an idea of the distortion caused by the absorption spectrometer. In this way, the positions of the undistorted K $\beta_{1,3}$ lines for the absorption spectrometer were obtained and could be aligned with the corresponding lines for the emission spectrometer.

All the XES and XAS K bands presented in the following figures were cleared of the apparatus smearing (via deconvoluting the measured curves by corresponding apparatus smearing functions) and, therefore, alignment of the energy scales for the absorption and emission spectrometers via the maxima of the undistorted calibration K $\beta_{1,3}$ lines of relevant elements was possible. Note that this procedure allows us to align the experimental x-ray emission and x-ray absorption spectra of the same element in a compound. Matching the spectra of different elements cannot be done in this way.

2.3. Calculations

Theoretical x-ray emission and absorption spectra of CuGaSe₂ and ZnGeAs₂ were published in [1, 2], where more details about the calculational procedure can also be found. Here we note only that our calculations were based on an *ab initio* local density approximation (LDA) scheme. The x-ray emission spectra shown here were obtained via an all-electron full potential band-structure calculation based on a pseudopotential technique. The x-ray absorption spectra shown here were obtained via a real-space multiple-scattering (RSMS) method involving a self-consistent muffin-tin potential and a relaxed and screened core hole.

3. Results

Our results are summarized in figures 2 and 3. The alignment of all the spectral curves was achieved by a combined experimental–theoretical method. In particular, the procedure described in section 2.2 enabled us to align the x-ray emission and x-ray absorption spectra of the same element solely by relying on the experiment. Matching of the spectra for *different* elements, on the other hand, was provided by the theory: the positions of the calculated x-ray emission bands are well-defined since they follow from a band-structure calculation. The very good agreement between the theory and the experiment then makes it possible to align the experimental x-ray emission bands with the theoretical x-ray emission bands (more details and justifications can be found in [1]).

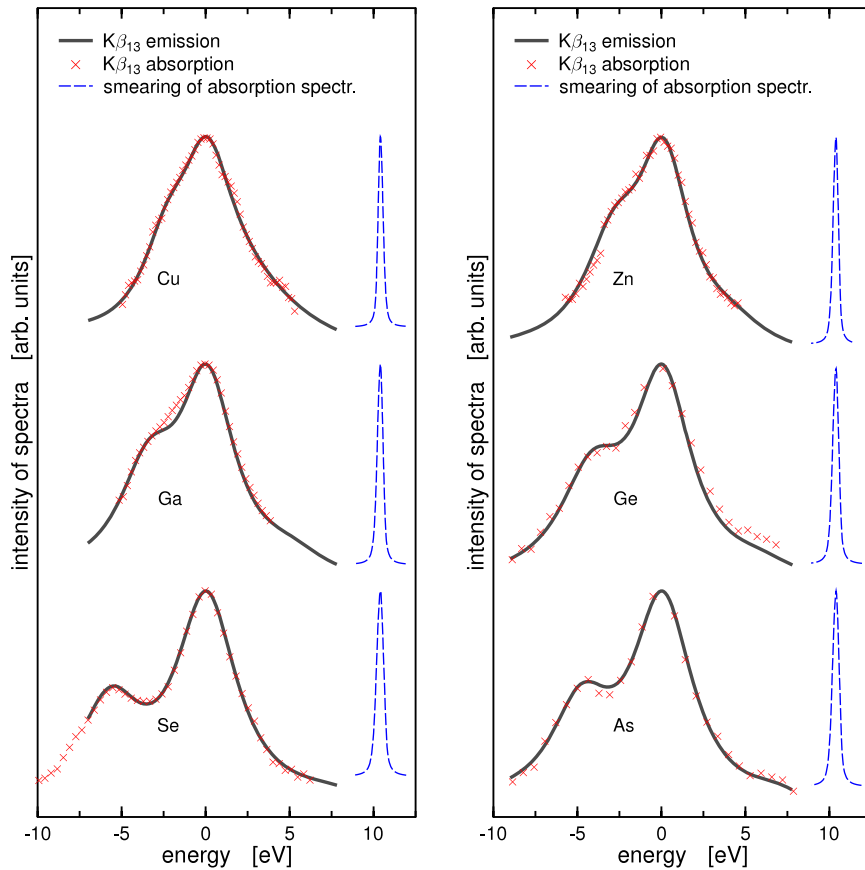


Figure 1. Calibration $K\beta_{1,3}$ lines of CuGaSe_2 (left panel) and ZnGeAs_2 (right panel) measured in the absorption spectrometer (crosses) together with the undistorted $K\beta_{1,3}$ line convoluted by the smearing function of the absorption spectrometer (full lines). The intensities of the lines were normalized to a common value, the positions of the measured and convoluted $K\beta_{1,3}$ lines were mutually aligned. The apparatus smearing functions of the absorption spectrometer for each $K\beta_{1,3}$ line are shown via a dashed line for each of the elements.

The matching of the theoretical x-ray absorption bands to the experiment was done by hand, by shifting the positions of all three theoretical bands by the same amount (such a procedure is analogous to applying the so-called ‘scissors operator’ [7, 8], which corrects for the deficiency of the LDA to reproduce the gap in semiconductors). The mutual alignment of the theoretical x-ray absorption bands for different elements of the same compound was thus provided by the theory itself (see also [2]).

4. Discussion

Our aim was to experimentally align XES and XAS and, with additional help provided by calculated XES, to match the x-ray emission and x-ray absorption spectra of different elements constituting the studied ternary semiconductors. The good agreement concerning the positions of the measured and the calculated x-ray absorption bands indicates that our procedure is reliable (it should be noted that the theoretical x-ray emission and x-ray absorption spectra presented in figures 2 and 3 were obtained from different calculations).

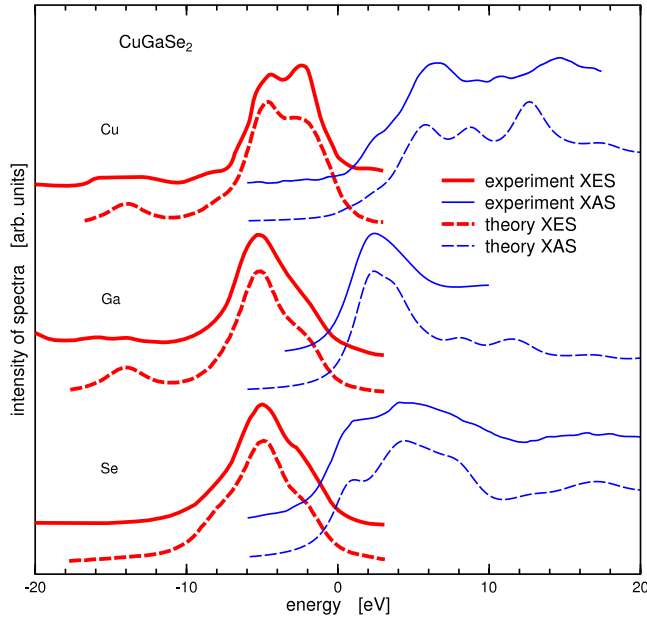
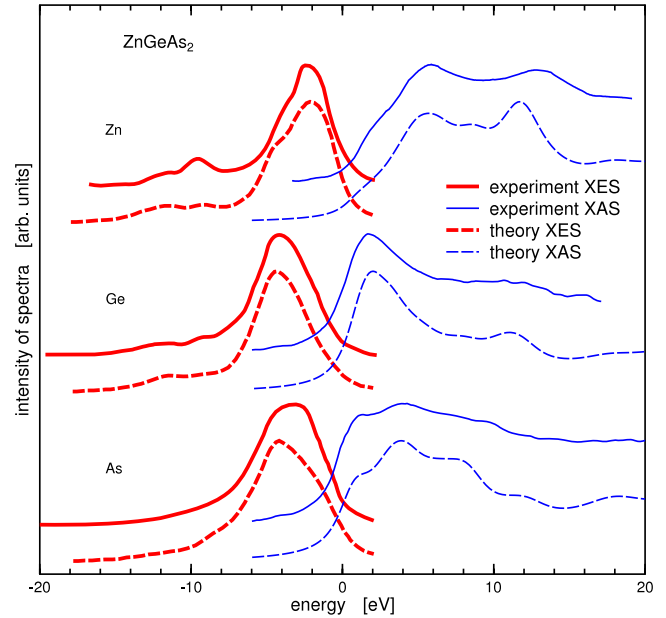
Having the XES and XAS bands aligned on the same energy scale makes it possible to observe an ‘element-specific gap’ in the p states for CuGaSe_2 and ZnGeAs_2 . An estimate of the gap can be semiquantitative only; the situation

is complicated by the gentle slopes of the onsets of the absorption and emission bands resulting from the short 1s core hole lifetime and, additionally, by the autoabsorption (which depletes the intensity of the recorded XES for energies close to the onset of the x-ray absorption band). Therefore, we do not attempt to assign any particular numerical values to the local p gaps on the basis of figures 2 and 3. Nevertheless, a clear trend to *decrease* the gap in the locally projected p states when going from the cations to the anions still can be seen. Moreover, the local p gap appears to correlate with the electronegativity of the corresponding element: elements with a higher electronegativity have a smaller locally projected p gap (compare figures 2 and 3 with table 1). The difference between the locally p-projected gaps in cations and in anions would be even more pronounced if correction for the autoabsorption in the emission bands could be accounted for. However, as the excitation of the emission bands was done using a continuous spectrum it is not possible to model the autoabsorption reliably enough. This deficiency could be overcome by employing monochromatic x-ray radiation to excite the x-ray emission spectra.

The optical gaps in CuGaSe_2 and ZnGeAs_2 are 1.68 and 1.15 eV, respectively [9]. The gaps in the x-ray spectra, on the other hand, are considerably smaller: the first features in XAS appear at around 0.9 eV above the top of the valence

Table 1. Pauling, Allred–Rochow and Phillips electronegativities of elements constituting the ternary semiconductors CuGaSe₂ and ZnGeAs₂ [19, 20].

CuGaSe ₂				ZnGeAs ₂			
Element	Pauling	Allred–Rochow	Phillips	Element	Pauling	Allred–Rochow	Phillips
Cu	1.9	1.75	0.79	Zn	1.6	1.66	0.91
Ga	1.6	1.82	1.13	Ge	1.8	2.02	1.35
Se	2.4	2.48	1.79	As	2.0	2.20	1.57

**Figure 2.** Experimental and theoretical x-ray emission and x-ray absorption spectra of CuGaSe₂, aligned on the same energy scale. The energy zero corresponds to the top of the valence band in the calculation.**Figure 3.** Experimental and theoretical x-ray emission and x-ray absorption spectra of ZnGeAs₂, aligned on the same energy scale. This plot is analogous to figure 2.

band for Se and As spectra (see figures 2 and 3). This contraction of the gap is apparently caused by the 1s core hole. Note that the core hole only has a small influence on the positions of the x-ray emission bands but it affects the positions of the x-ray absorption bands (assuming the validity of the so-called final-state approximation [10]). The energy separation between the valence states and the core hole-influenced conduction states is thus decreased with respect to the case of optical spectroscopy, where no core hole is present. To calculate this shift accurately is a difficult task because it requires accounting for the dynamics of the creation of the core hole in a solid. Recently, Shirley [11] applied the Bethe–Salpeter approach to Ti K-edge XAS of rutile TiO₂ and found that including the electron–core hole interaction shifts the onset of the x-ray absorption spectrum by about 0.5 eV to lower energies. This value is in the same range as that needed to explain the apparent disagreement between the x-ray gaps shown in figures 2 and 3 and the tabulated optical gaps. Further, the fact that the positions of our experimental and theoretical x-ray absorption bands agree indicates that the contraction of the gap caused by the 1s core hole is about the same for all three elements constituting CuGaSe₂ and ZnGeAs₂. This is plausible, because all these elements have similar atomic numbers Z (between 29 and 34).

The existence of a relation between the locally projected p gap and the electronegativity can be seen as a hint that electronegativity is a viable concept in interpreting the electronic structure of chalcogenide and pnictide semiconductors. To our knowledge, a correlation like this has not been observed before. One of the reasons may be that accurate alignment of experimental x-ray emission and x-ray absorption spectra is quite a difficult task, usually requiring significant rearrangements of the apparatus. Nevertheless, alignment of some edges of the compound has been obtained for similar systems in the past. For example, emission and absorption spectra at the P edges of ternary phosphides MgSiP₂, ZnSiP₂ and CdSiP₂, were aligned by means of the P K α line and L_{2,3} bands of silicon were superimposed on them using x-ray electron spectroscopic data [12]. Similarly, the S K- and L-edges of several binary and ternary sulfides (including CuGaS₂, AgGaS₂ and AgAsS₂) were juxtaposed by Lavrentiev *et al* [13, 14]. A situation somewhat analogous to ours can be found in the work on semiconducting ternary sulfides [15] where the local p gap for S and for P was determined for TI₃PS₄. The electronegativity of P is smaller than the electronegativity of S and, in agreement with the trend observed by us, the gap for P was found to be larger than the gap for S.

Local angular-momentum-projected gaps in delafossites CuGaO₂ and CuInO₂ can be estimated from the Cu L₃, Ga L₃, In M₅, and O K emission and absorption spectra aligned via the core level binding energies [16]. In this case, a clear relationship between the local gap and electronegativity cannot be observed. One should note, however, that several symmetries are being mixed in the work on the delafossites (the local gap concerns the s and d states for Cu and Ga, the p and f states for In and the p states for O), whereas in our situation only the p symmetry states are involved. Besides, it is not quite clear to what degree the fluorescence yield mode and alignment via photoemission core binding energies used in [16] are equivalent to our procedure in a situation where a high accuracy is required.

Another interesting comparison can be made with CuInSe₂, which is a close analogue to CuGaSe₂. Absorption spectra at all the K-edges were measured and calculated by Bacewicz *et al* [17]. One observes by comparing our figure 2 with figure 5 of [17] that the shapes of the individual spectra at analogous edges of CuGaSe₂ and of CuInSe₂ are quite similar and that, moreover, the mutual positions of the edges also agree (the Se edge is lowest in energy, then comes the Ga or the In edge, and the Cu edge is located at yet higher energies). Although this agreement is remarkable, one cannot properly assess its significance because, unfortunately, it is not mentioned explicitly in [17] how the alignment of the Cu, In and Se edges was achieved. It may have come from the calculations (analogously to our theoretical XAS curves) but it may also have been set so that a visual correspondence between prominent peaks is established. In any case this indicates that it would be interesting to see to what extent such a correlation between edge positions occurs for other systems as well.

It should be emphasized that the local p gap visualized in figures 2 and 3 is *not* the 'standard' energy gap usually employed in semiconductor physics. It is connected with the local aspects of the electronic structure, thus offering a view of the energy gap from a different perspective to that provided by optical absorption, wavelength derivative spectroscopy or electroreflectance measurements. Note that the local p gap cannot be probed directly by radiative transitions (despite its spectroscopic character), because transitions between p states are dipole forbidden. It can be accessed only indirectly, such as by the procedure used by us. The specific character of the local p gap explored by x-ray spectroscopy also means that concepts which are known to work for common energy gap need not be applicable to our case (such as, for example, the bowing effect in semiconducting alloys [18]).

Good agreement between the positions of the theoretical and experimental x-ray absorption bands in figures 2 and 3 can be seen as an *a posteriori* verification of the alignment procedure described in section 2.2. From another point of view, one can see this agreement as a justification for applying the scissors operator [7, 8] to unoccupied states in ternary semiconductors; the LDA appears to be able to predict the mutual positions of XAS bands of different elements of the same compound correctly. This suggests that when attempts are made to align XAS spectra at several edges of the same compound, LDA calculation may serve

as a good guide. It is worth noting that our calculated results are not dependent on any specific method; we showed earlier that the real-space multiple-scattering formalism and the pseudopotential method yield essentially similar results for XAS [2, 21].

Combined x-ray emission and x-ray absorption spectroscopies are a unique tool for investigating the electronic structure of solids because together they give access to both occupied *and* unoccupied states projected in an element- and angular-momentum-specific way. A reliable and accurate procedure for mutual alignment of the x-ray emission and the x-ray absorption bands is a necessary prerequisite for exploiting the full potential of both spectroscopies.

5. Conclusions

Due to the possibility of calculating the apparatus smearing function of the two-crystal spectrometer, the x-ray emission and x-ray absorption spectra of all the elements constituting a ternary semiconductor can be mutually aligned via the K $\beta_{1,3}$ calibration line measured by the emission and by the absorption spectrometer. For CuGaSe₂ and ZnGeAs₂, the x-ray gap in the p states depends on the element onto which the states are projected; the gap decrease correlates with the electronegativity of the corresponding element. The mutual positions of x-ray absorption bands of different elements of the same ternary semiconductor can be correctly predicted within the LDA, provided that the scissors operator is applied to fix the onset of the conduction band.

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References

- [1] Drahokoupil J, Drbohlav I, Horák J, Polčík M and Šimůnek A 1997 *Solid State Commun.* **103** 303
- [2] Šipr O, Drahokoupil J, Machek P and Šimůnek A 2005 *Phys. Scr. T* **115** 179
- [3] Drahokoupil J and Fingerland A 1968 *Czech. J. Phys. B* **18** 1190
- [4] Drahokoupil J and Fingerland A 1982 *Advances in X-ray Spectroscopy* ed C Bonnelle and C Mande (Oxford: Pergamon) p 167
- [5] Burger H C and van Zitter P H 1927 *Z. Phys.* **44** 58
- [6] Burger H C and van Zitter P H 1932 *Z. Phys.* **79** 722
- [7] Godby R W, Schlüter M and Sham L J 1988 *Phys. Rev. B* **37** 10159
- [8] Sole R D and Girlanda R 1993 *Phys. Rev. B* **48** 11789
- [9] Dittrich H, Karl N, Kück S and Schock H W 2000 *Ternary Compounds, Organic Semiconductors (Landolt-Börnstein Group III Condensed Matter, vol 41E)* (Berlin: Springer)
- [10] von Barth U and Grossman G 1982 *Phys. Rev. B* **25** 5150
- [11] Shirley E L 2004 *J. Electron. Spectrosc. Relat. Phenom.* **136** 77
- [12] Gusatinskii A N, Bunin M A, Blokhin M A, Minin V I, Prochukhak V D and Averkieva G K 1980 *Phys. Status Solidi b* **100** 739

- [13] Lavrentyev A A, Nikiforov I Y and Gabrelian B V 1997 *J. Physique IV* **7** C2 283
- [14] Lavrentiev A A, Gabrel'yan B V, Nikiforov I Y and Vorzhev V B 2005 *J. Struct. Chem.* **46** 805
- [15] Lavrentyev A A, Gusatinskii A N, Nikiforov I Y, Popov A P and Ilyasov V V 1993 *J. Phys.: Condens. Matter* **5** 1447
- [16] Makhova L, Wett D, Lorenz M and Konovalov I 2006 *Phys. Status Solidi a* **203** 2861
- [17] Bacewicz R, Wolska A, Lawniczak-Jablonska K and Sainctavit P 2000 *J. Phys.: Condens. Matter* **12** 7371
- [18] Bernard J E and Zunger A 1987 *Phys. Rev. B* **36** 3199
- [19] Lof P 1987 *Elsevier's Periodic Table of the Elements* (Amsterdam: Elsevier)
- [20] Phillips J C 1970 *Rev. Mod. Phys.* **42** 317
- [21] Šipr O and Šimůnek A 2001 *J. Phys.: Condens. Matter* **13** 8519