Experimental and Theoretical $2p$ Core-Level Spectra of Size-Selected Gas-Phase Aluminum and Silicon Cluster Cations: Chemical Shifts, Geometric Structure, and Coordination-Dependent Screening

Supplementary Information

Michael Walter, Marlene Vogel, Vicente Zamudio-Bayer, Rebecka Lindblad, Thomas Reichenbach, Konstantin Hirsch, Andreas Langenberg, Jochen Rittmann, Alexander Kulesza, Roland Mitrić, Michael Moseler, Thomas Möller, Bernd von Issendorff, and J. Tobias Lau

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Parameters for the global optimization of silicon cluster cations

We use the nomenclature of Vilhelmsen and Hammer[1] in the following. A population size of 20 was employed for all cluster sizes. The cut-and-splice operator was used for pairing with a mutation probability of 0.2, where mirror and rattle mutations occurred with equal probability. In order to ensure diversity in the population an inter-atomic distance comparator was used with the comparison parameters $\delta_{\mathrm{rel}} = 0.015$ Å, $\Delta E = 0.02$ eV and $d_{max} = 0.7$ Å.

$2p$ binding energy and structural parameters in silicon clusters

Bulk silicon was set up in a diamond cubic crystal structure with a lattice constant of 5.43 Å.[2] The corresponding coordination parameter c shows a large plateau between 2.5 and 3.5 Å as shown in Fig. S1a). We choose $R = 3$ Å and $dR = 0.2$ Å for the coordination analysis presented in fig. S1b). As suggested by

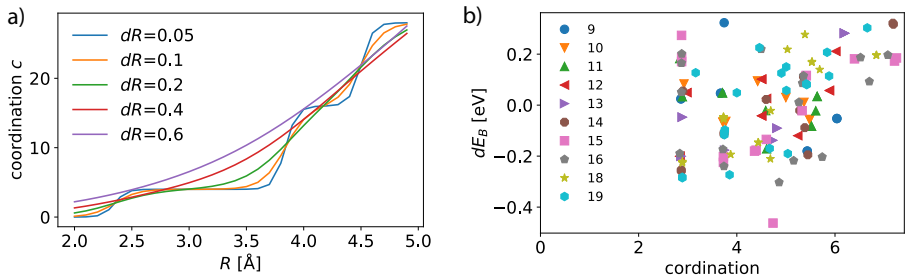


Figure S1: a) Behavior of coordination number c with R and dR for bulk silicon. b) $2p$ binding energy difference dE_B versus c for silicon clusters. The number of silicon atoms in the cluster is given in the legend.

the analysis presented in Fig. 3 of the main text, there is no obvious correlation between coordination number and $2p$ binding energy visible for silicon clusters.

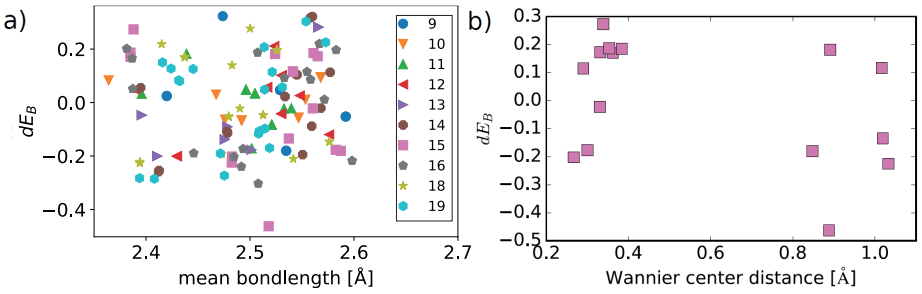


Figure S2: a) $2p$ binding energy difference dE_B versus mean bond length for silicon clusters. The number of silicon atoms in the cluster is given in the legend. b) $2p$ binding energy difference dE_B versus minimal distance of the center of the Wannier function to the atom that is ionized in Si_{15}^+.

Yazyev and Pasquarello[3] found a correlation between bond length or Wannier orbital centers[4–6] and Si $2p$ core-level shifts for silicon surfaces. We therefore searched for simple correlations of these quantities to the $2p$ binding energy difference dE_B in silicon clusters. As can be seen in Fig. S2, neither bond length nor the related distance of the Wannier orbitals' center correlate in a simple way with the $2p$ binding energy differences in clusters.

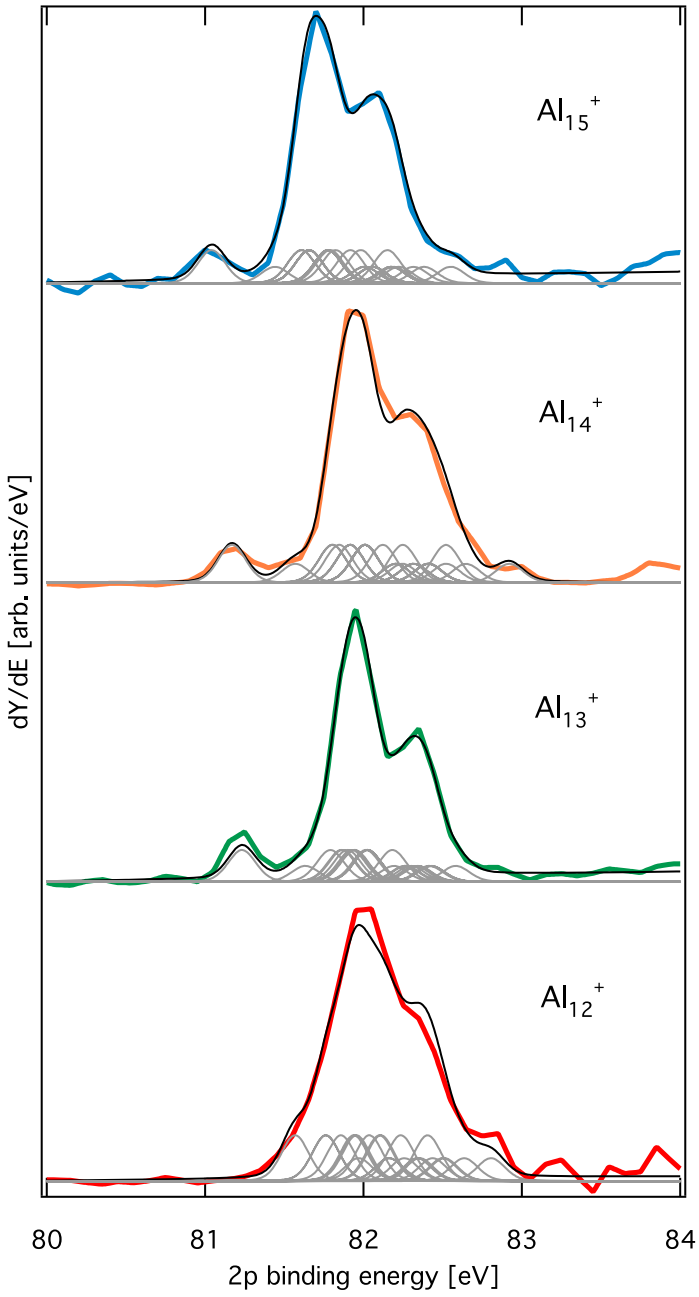


Figure S3: Fit of the experimental $2p$ binding energy spectra for Al_n^+ clusters with $n = 12 - 15$. Thin grey lines indicate the Voigt peaks for each atom used in the fitting of the experimental spectra and thin black line is the resulting fit.

Surface core-level shifts of Al(111) and Al(100)

Aluminum bulk and aluminum surfaces were set up in FCC symmetry with the experimental aluminum lattice constant of 4.05 Å [2].

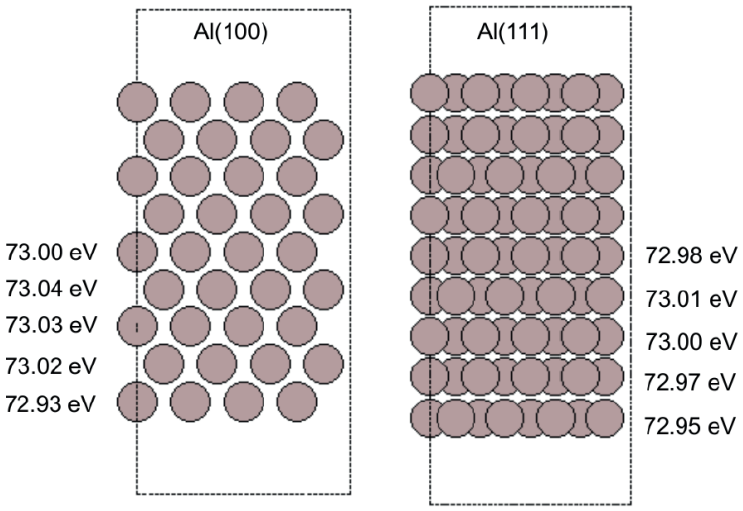


Figure S4: Unit cells and Al($2p$) binding energies of our models for the 100 and 111 surfaces of aluminum. Core hole energies are given at each layer and are equal throughout the layer.

Fig. S4 shows the unit cells used for modelling the Al(100) and Al(111) surfaces of aluminum. 5 Å vacuum were added to the unit cell in the direction of the surface normal and Dirichlet boundary conditions were applied in this direction, while periodic boundary conditions were applied otherwise. The slabs were allowed to relax to the nearest minimum without any symmetry restriction using 3×3 k-points to sample the Brillouin zone. Periodic calculations require charge neutral unit cells. We have neutralized the system containing a core hole by an additional electron in the valence band of the system. Core hole energies were calculated with a more dense sampling of 5×5 k-points. With this setting, the central layers of the slabs differ with less than 20 meV. While the variation of $2p$ energies is ~ 100 meV in Al(100) it is found to be only the ~ 50 meV in Al(111) in agreement with literature [7].

Offset δ to calculated binding energies

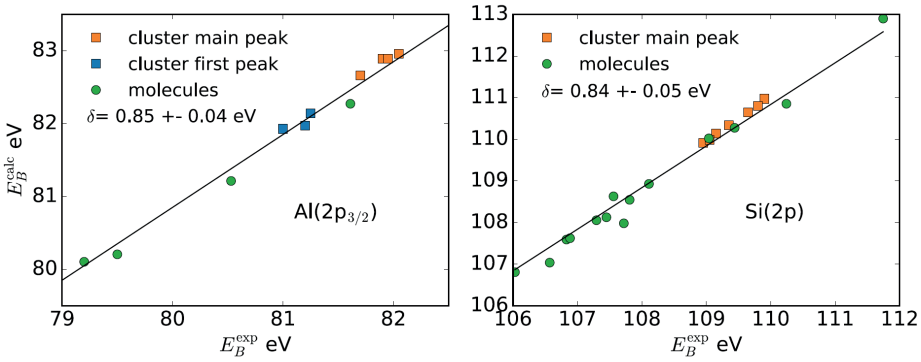
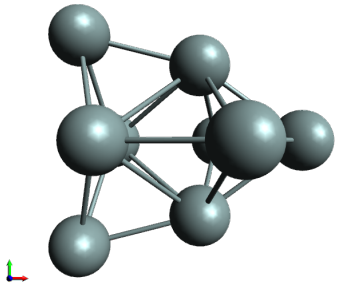


Figure S5: Calculated $2p$ core electron binding energies pre-δ corrections versus to molecular[8] and cluster data. The constant offsets δ for Al and Si corresponding to the straight line are given.

As discussed in[9], the selection of molecules or complexes used in the fit required to determine δ was rather limited in particular for Al, where only four complexes could be taken into account. We may also use, in addition to the molecular data, the experimental data of the cluster cations to improve the fit and to obtain more general values of δ. In case of aluminum, we use the positions of two distinct peaks for this purpose, i.e. the low energy peak of Al^+_{13-15} and the main peak of Al^+_{12-15}. Both peaks can be assigned to pure Al $2p_{3/2}$ contributions as we have checked from our calculated values. The correlation between experimental and raw calculated values of the cations aligns nicely to the neutral molecular complexes as shown in Fig. S5. Similarly, for Si $2p$, we also take the experimental cluster data into account in the fitting procedure. We use the main peaks of the best matching structures Si^+_{9-13} and $Si^+_{15,16}$ for this purpose. Similarly to aluminum, these peaks can be shown to be purely $2p_{3/2}$ contributions. The experimental peak positions are corrected for the spin-orbit splitting as we are fitting to the spin-averaged Si $2p$ (there is most molecular data available for this value[8]).

xyz coordinates of silicon cluster cations

9



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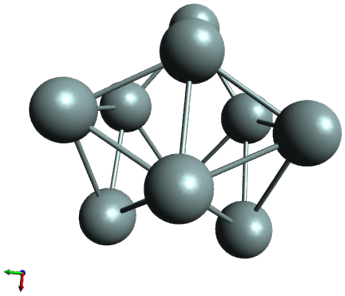

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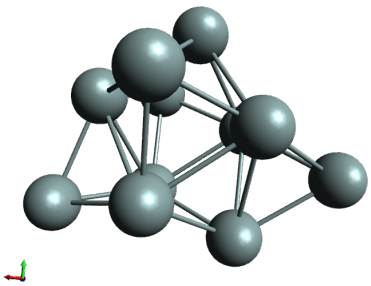

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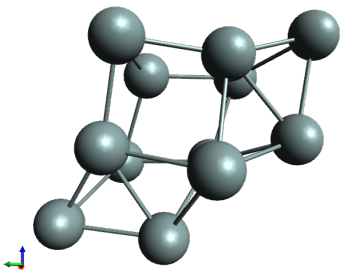

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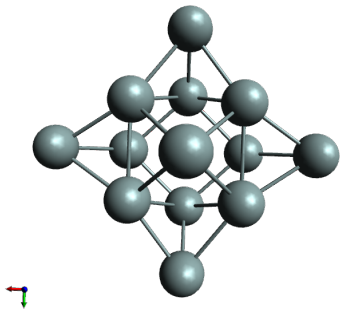

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14

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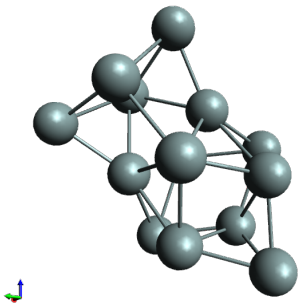

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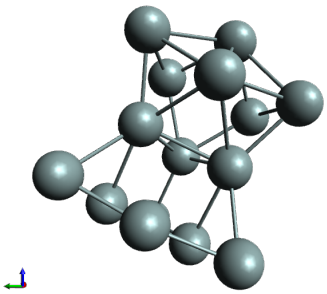
15-A



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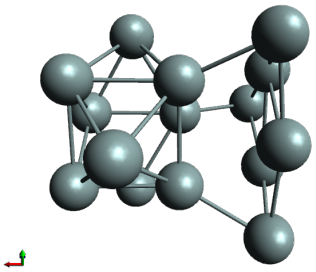
15-B



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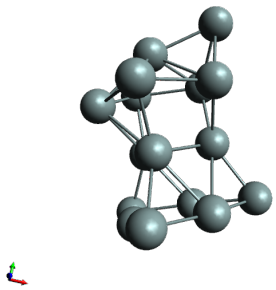
16-A



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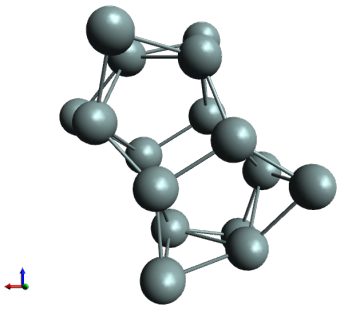
16-B



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18-A

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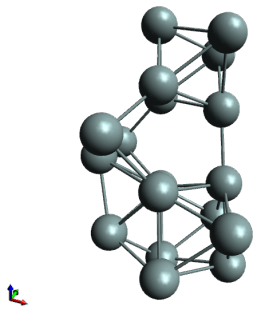

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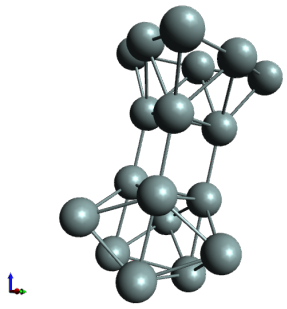
18-B



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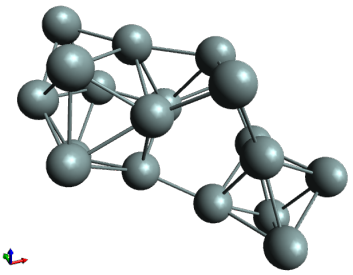
19-A



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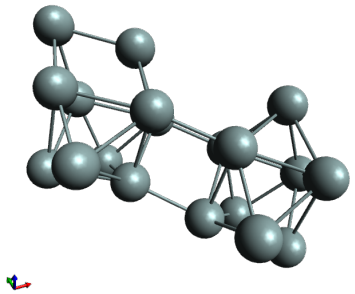
19-B



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19-C
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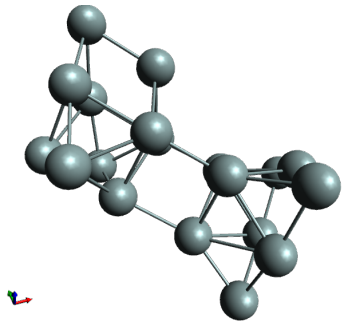

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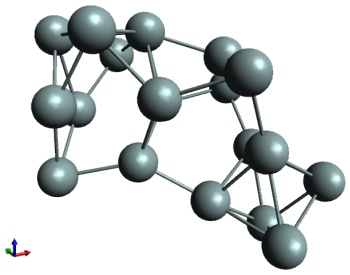
19-D



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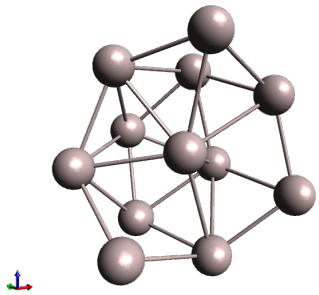
Si 8.30330000 5.36030000 9.91230000
Si 10.29350000 9.04450000 8.09270000
Si 8.97980000 5.21760000 7.62280000
Si 10.04200000 7.13430000 6.66820000
Si 9.99190000 6.12420000 4.35760000
Si 11.01360000 4.91280000 6.28380000
Si 8.85050000 4.05870000 5.39000000
Si 7.98890000 6.32640000 5.75680000
Si 7.24100000 8.96730000 10.31650000
Si 5.37610000 10.27160000 7.75480000

Si 4.24000000 8.33040000 8.75950000
Si 7.14420000 11.14110000 9.12090000
Si 5.21520000 7.63970000 10.84310000
Si 4.91440000 10.21660000 10.22210000
Si 7.90920000 9.18920000 7.85840000
Si 6.63210000 6.84370000 9.02760000
Si 4.18780000 8.70780000 6.40550000
Si 6.32890000 7.71140000 6.81020000

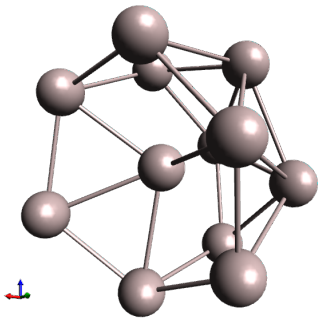
xyz coordinates of aluminum cluster cations

12-A



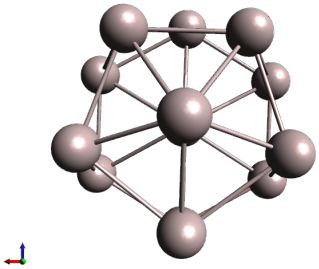
Al 6.12483 5.36710 6.73275
Al 8.20948 6.87295 5.95633
Al 5.13613 6.96380 8.73438
Al 4.08805 7.15557 6.28438
Al 6.34063 8.55044 6.88841
Al 4.31610 5.21908 4.56129
Al 8.56374 4.92652 8.01416
Al 8.68794 4.22892 5.54620
Al 6.42834 4.83677 9.49505
Al 7.82870 7.36332 8.59171
Al 6.07484 7.68208 4.49938
Al 6.86642 5.24116 4.04478

12-B
Al -0.0617335 -0.7929182 -0.4629581
Al -2.3522906 -1.8739716 0.4888191
Al -1.3945083 0.5147432 1.7249816
Al -2.5127140 0.6718646 -0.8000845
Al 0.0260897 1.9080021 -0.3241330
Al -2.3226336 -1.6541278 -2.0912367
Al 1.9430750 -1.7027316 1.1460657



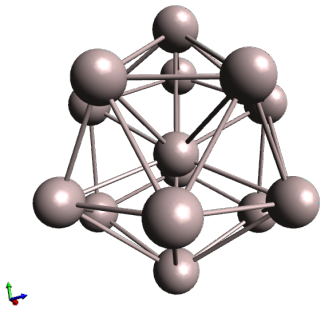
Al 1.9625982 -2.2697482 -1.4603195
Al -0.4124814 -1.9174469 2.2045338
Al 1.2597123 0.7486901 1.6343311
Al -0.6438633 1.0304812 -2.6654489
Al 0.0466246 -1.4257028 -3.1132865

13



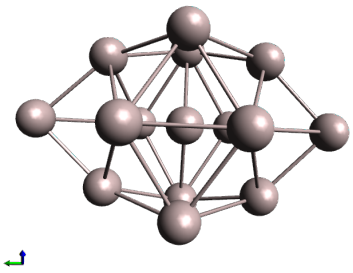
Al 6.41301036 5.07773508 6.83359116
Al 4.08088351 4.21650757 8.01844691
Al 8.67725591 6.74486814 6.38338384
Al 5.02202419 6.58399799 8.84475186
Al 4.20180863 6.77663394 6.26342011
Al 6.43010348 7.88648660 7.05075466
Al 4.19247176 4.29671807 5.40532880
Al 8.63297724 4.16550240 8.18434736
Al 8.71426540 4.25234736 5.57000339
Al 6.30902360 4.15001422 9.41499242
Al 7.70792833 6.55824128 8.92302003
Al 6.48168264 6.92802783 4.64953923
Al 6.50198738 4.36226859 4.18308494

14



Al 6.82047000 6.59684000 6.98758000
Al 4.74188000 4.77016600 7.53891400
Al 9.31664100 7.04137200 6.08002000
Al 5.23255100 7.11562500 9.13150500
Al 4.26926400 7.46585100 6.63870400
Al 6.06299100 9.17523800 7.64173000
Al 5.19822000 5.62680100 4.98517800
Al 9.15184000 5.37614700 8.11180100
Al 7.37221200 4.13095000 6.42445100
Al 6.85395900 5.03066600 9.25212500
Al 8.02908700 7.73164200 8.98930700
Al 6.51052300 8.29289500 5.04061700
Al 7.68983200 5.90930300 4.34957700
Al 8.51064200 9.45219300 6.74806300

15



Al 8.00524500 5.79420900 8.02465200
Al 8.05430800 9.98905800 8.12911400
Al 4.12237400 8.03601500 6.25465800
Al 8.45632700 9.38057900 5.28643900
Al 5.15312300 6.50235800 8.30824100
Al 8.38974000 6.54160400 5.19580600

Al 5.20400900 9.34131100 8.41208900
Al 5.50894400 5.93843800 5.42857700
Al 6.80025200 7.93382200 6.79916000
Al 6.36073600 8.06472500 4.10467700
Al 5.63344000 10.12505500 5.61655300
Al 6.89100700 11.92222200 6.92968600
Al 6.72411000 4.07611500 6.65993200
Al 7.24263900 7.85905100 9.49536400
Al 9.47622900 7.88649900 7.34925900

References

[1] L. B. Vilhelmsen and B. Hammer, *The Journal of Chemical Physics*, 2014, **141**, 044711.

[2] *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide, CRC Press, Boca Raton, 85th edn., 2004.

[3] O. V. Yazyev and A. Pasquarello, *Physical Review Letters*, 2006, **96**, 157601.

[4] K. S. Thygesen, L. B. Hansen and K. W. Jacobsen, *Physical Review B*, 2005, **72**, 125119.

[5] J. Enkovaara, C. Rostgaard, J. J. Mortensen, J. Chen, M. Dułak, L. Ferrighi, J. Gavnholt, C. Glinsvad, V. Haikola, H. A. Hansen, H. H. Kristoffersen, M. Kuisma, A. H. Larsen, L. Lehtovaara, M. Ljungberg, O. Lopez-Acevedo, P. G. Moses, J. Ojanen, T. Olsen, V. Petzold, N. A. Romero, J. Stausholm-Møller, M. Strange, G. A. Tritsaris, M. Vanin, M. Walter, B. Hammer, H. Häkkinen, G. K. H. Madsen, R. M. Nieminen, J. K. Nørskov, M. Puska, T. T. Rantala, J. Schiøtz, K. S. Thygesen and K. W. Jacobsen, *Journal of Physics: Condensed Matter*, 2010, **22**, 253202.

[6] N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza and D. Vanderbilt, *Reviews of Modern Physics*, 2012, **84**, 1419.

[7] M. Borg, M. Birgersson, M. Smedh, A. Mikkelsen, D. L. Adams, R. Nyholm, C.-O. Almbladh and J. N. Andersen, *Physical Review B*, 2004, **69**, 235418.

[8] W. L. Jolly, K. D. Bomben and C. J. Eyermann, *Atomic Data and Nuclear Data Tables*, 1984, **31**, 433.

[9] M. Walter, M. Moseler and L. Pastewka, *Phys. Rev. B*, 2016, **94**, 041112(R).