Electronic Supplementary Material (ESI) for: Optoelectronic properties and color chemistry of native point defects in Al:ZnO transparent conductive oxide

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Effect of DFT+U

The DFT description of ZnO bulk band structure provides a severe underestimation of the bandgap (E_g^{DFT}=0.7eV vs E_g^{exp}=3.3eV), well beyond the standard gap reduction given by DFT [1]. In particular, the wrong energy position of the Zn *3d* orbitals in the pseudopotential description causes a spurious interaction with the *sp* band of oxygen, which overestimates the covalent character of the Zn-O bonds in spite of its intrinsic polar component. This is responsible for the strong underestimation of the energy gap.

One possible and computationally inexpensive way to correct this behavior is to include an *ad hoc* Hubbard potential within the DFT+U scheme, as initially proposed by Janotti and co-workers [2]. In this framework, the Hubbard U values included in the calculations do not have to be considered as physical on-site electron-electron screened potentials, in the sense of the many-body Hubbard Hamiltonian, but as an unscreened parameters introduced to correct the gap.

An important issue within the DFT+U approach is the choice of the parameter U, for which no rigorous prescription exists. In the original work by Janotti and coworkers[2], the authors estimated a U value for the isolated Zn atom (U_{at}=18 eV), and corrected it with a parametrized value for the dielectric function of ZnO, in order to take into account the electronic differences between the atomic Zn and Zn within the ZnO environment. They obtained a final U parameter for Zn d-shell equal to 4.7 eV and an opening of the band gap of ZnO to 1.5 eV.

However, this partial opening of the gap is not enough for a reasonable simulation of the optical properties of ZnO and AZO compounds. The choice we did is different. Since the electronic properties of the separated Zn and O elements are very different from those of the ZnO compound we decided to derive U directly from the solid. In this case, due to the strong polarization of the Zn-O bond and the partial charge transfer from Zn-to-O, we applied the U correction to both elements in order to have a precise simulation of the bandstructure and the of bandgap of the system. By fitting the experimental ZnO bulk band structure [1], we obtained an Hubbard potential U=12.0 eV for the *3d* orbitals of zinc and U=6.5 eV for the *2p* orbitals of oxygen. This procedure has been adopted by many authors, providing very similar values for the used U parameters as well as very similar corrections to the electronic structure.[3–6] With respect to Janotti et al, we obtained a further bandgap opening of 1.5

eV, so to obtain the experimental value. Qualitatively, a larger bandgap is ascribable to an increase of the internal bond polarization and a higher localization of the electron density, thus an enhancement of the resulting Us is not surprising. A detailed set of accuracy tests on the effect of DFT+U (same set of parameters) on the electronic structure of both ZnO bulk and surfaces can be found in Refs [7, 8]. It is important to note that the inclusion of Hubbard potential, by correcting the Zn–O hybridization, properly describes not only the electronic structure but also the vibrational and dielectric properties of ZnO, in agreement with the experimental results (e.g. Raman, IR) [9].

In order to show the effect of inclusion of U in the case of undefective AZO, we compared the density of states (DOS) obtained with and without the inclusion of U. The results are summarized in Fig. S1. The effect of the Hubbard correction is firstly to decouple the Zn(3d) and O(2p) band and consequently to open the gap exactly of the same extent of the undoped ZnO case. We note also that the inclusion of U does not modify or the n-doping process due to Al impurities, which donates their *3p* electrons to the host, filling the bottom of the ZnO conduction band.

Evidently, since in the case of pure DFT (no U correction) the dramatic underestimation of gap makes the original ZnO unphysically absorbing light in the IR-vis range (rather than in the UV), also the corresponding Al-doped system does not represent a transparent material. This explains the need for introducing the bandgap correction described above to describe the optoelectronic properties of the compound.

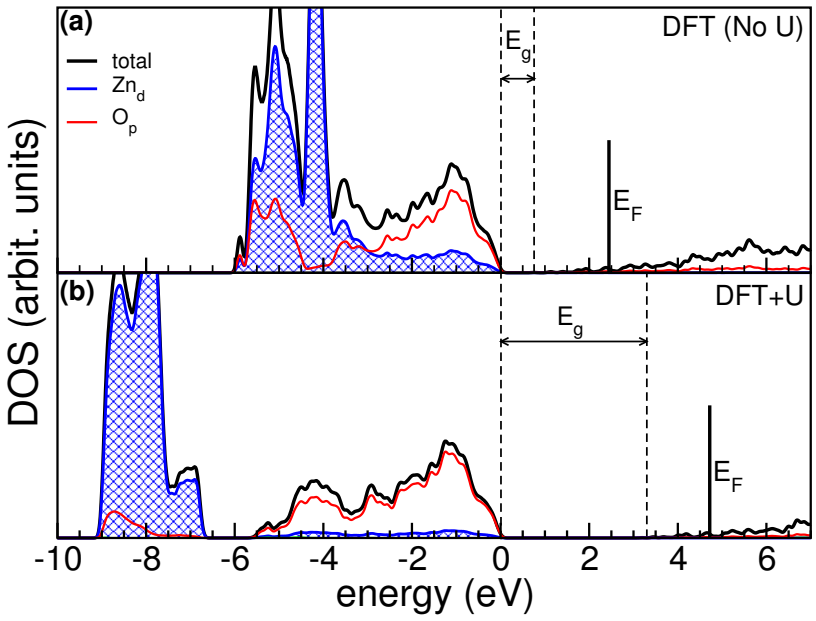

FIG. S1: DOS of undefective AZO bulk without (a) and with (b) the inclusion of Hubbard U correction. Black lines represent the total DOS, while blue shaded areas and red thin lines identify the contribution of *3d* electrosn of zinc and the *2p* electrons of oxygen, respectively. Zero energy reference is set to the top of valence band of the pristine ZnO host. Dashed vertical lines mark the energy gap (E_g) and thick black lines the resulting Fermi levels (E_F) of AZO system.

Relaxed atomic structures

Figure S2 shows the 3D view of relaxed geometries of AZO (3.2%) bulk in the presence of defects, discussed in the main text. In all cases the simulation cell is (in Å):
(6.577, 0.000, 0.000)
(0.000, 11,392, 0.000)
(0.000, 0.000, 10.629).

Simulations of AZO (1.6%) and simulations with different Al-to-vacancy ratio (see next section) have been performed doubling the cell along the x direction. The XYZ coordinates for all AZO (3.2%) structures are listed at the end of this file.

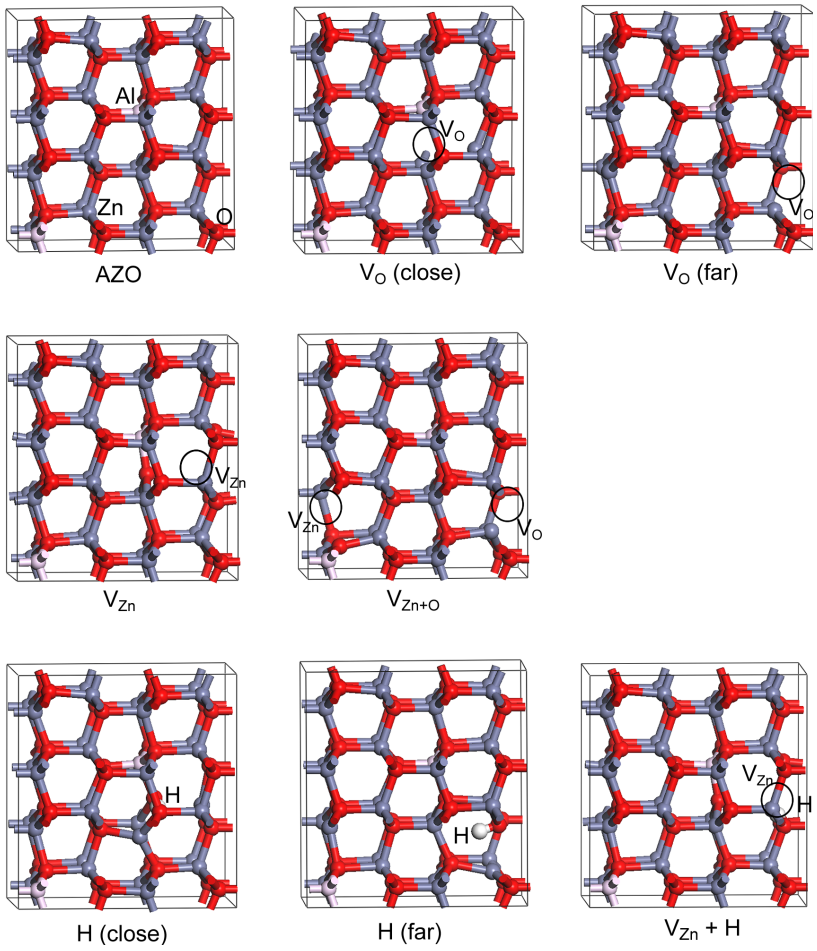

FIG. S2: 3D atomic structures of optimized AZO bulk in the presence of no defects, oxygen vacancies (V_O), zinc (V_{Zn}) and zinc-oxygen dimer (V_{Zn+O}) vacancies and hydrogen impurities. Labels refer to main text. Open circles identify the position of vacant atoms. Grey, red, and pink spheres represent Zn, O and Al atoms, respectively.

Modification of Al and defect contents

We checked the robustness of our results with respect to the modification of the Al amount and/or the ratio between Zn vacancies and Al impurities. Figure S3 shows the comparison between AZO with 3.2% (as in the main text) and 1.6% of Al content, in the presence of oxygen vacancies, in the *close* and *far* configurations (see main text for labels). AZO (1.6%) has been obtained by using the same simulation cell (64 atoms), but in the presence of a single Al/Zn substitution (1/64$\sim$ 1.6%). The structures are then fully relaxed.

For both *close* and *far* systems, the results confirm what observed for the 3.2% case

(Figure 1, main text): oxygen vacancies introduce deep and fully occupied in-gap state, while they do not directly interact with the Al dopant that donates its valence electron to the ZnO conduction band, imparting a TCO character to the system. The only expected differences observed between the two doping cases is the final position of the Fermi level that results deeper inside the conduction band in the case of higher Al amount (3.2 %), because higher is the free electron charge injected in the host.

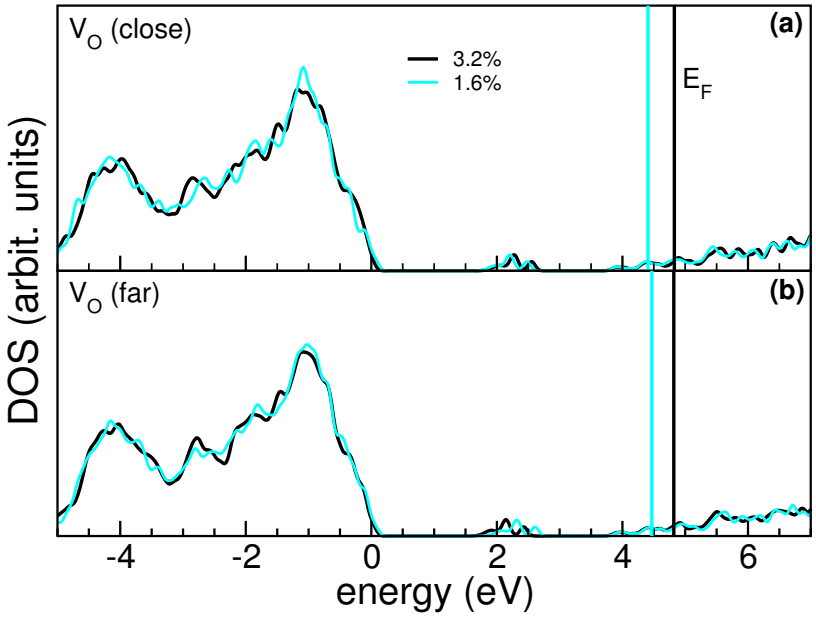

FIG. S3: DOS plots for AZO bulk in the presence of oxygen vacancies (V_O) in (a) *close* and (b) *far* configurations at different Al content, namely 3.2% (black line) and 1.6% (cyan line). Black lines are the same of Fig. 1b, and reported for sake of clarity. Vertical lines identify the position of the corresponding Fermi levels. Zero energy reference is set at the top of valence band of the ZnO host.

Figure S4a shows the analogous case for AZO bulk in the presence of V_{Zn}, at different Al dosages (1.6 and 3.2%), but keeping fixed the ratio (1:2) between the number of Zn vacancies and of Al impurities. In this case the system has been simulated by using a doubled cell (128 atoms), including 2 Al ions in Zn-subsitutional sites (2/128$\sim$ 1.6%) and a single Zn-vacancy. As the compensation ratio (1:2) is maintained, the picture remains essentially the same, with the system that behaves as a semiconductor rather than a TCO.

Panels b and c display instead the case in which the formal doping is maintained at 3.2% (as in the main text), while the compensation ratio is changed. In one case (panel

b) the number of V_{Zn} is reduced with respect to the Al dopant, in the other (panel c) the reciprocal ratio is inverted. The former case (1:4), which physically corresponds to a high quality grown sample, is simulated by using a doubled cell (128 atoms), including 4 Al impurities (4/128$\sim$ 3.2%) and a single Zn vacancy. The latter, which corresponds to a highly defective sample, is obtained from the same simulation cell (128 atoms), including 4 Al impurities and three Zn vacancies.

The modification of the compensation ratio radically modifies the electrical character of the system that results semiconducting in vacancy rich conditions (panel c) while it restores the intrinsic TCO behavior of undefective AZO in Al rich conditions.

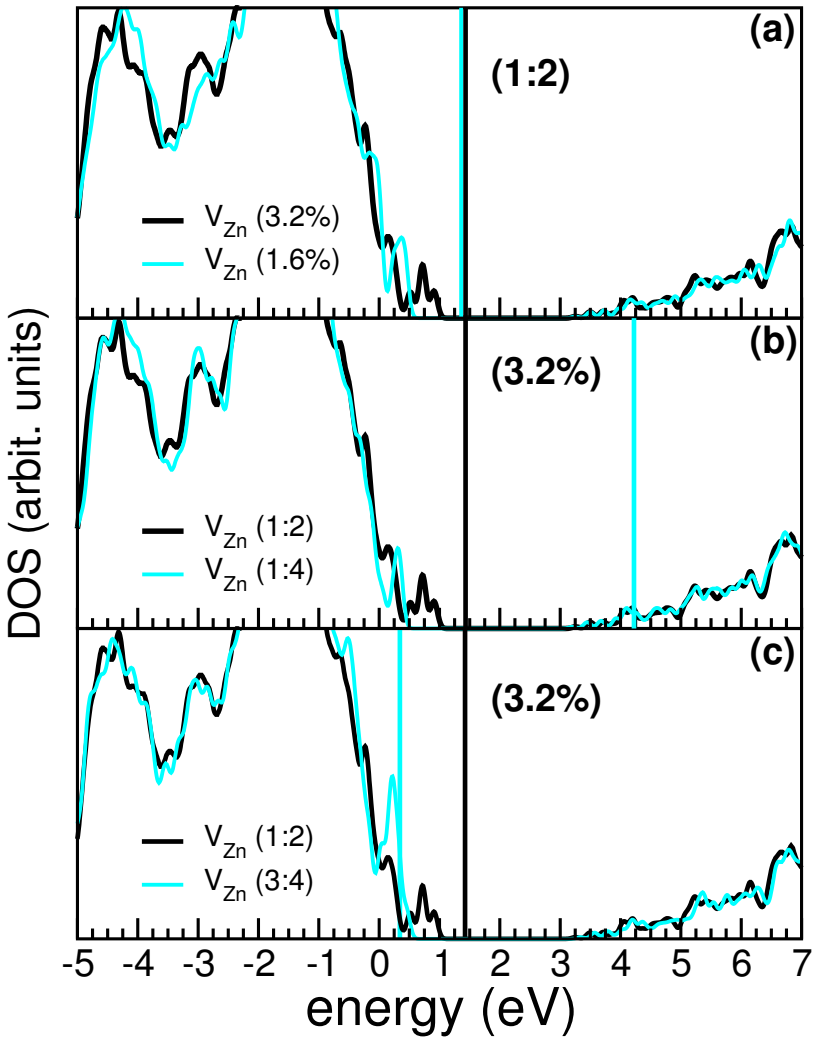

FIG. S4: DOS plots for AZO bulk in the presence of Zn vacancies (V_{Zn}). (a) Comparison between 1.6% (cyan)and 3.2% (black) Al content at fixed compensation ratio (1:2). (b-c) Comparison between different Zn vacancy-Al ratio, at fixed formal doping level (3.2%). Black line is the same of Fig. 1c (namely, one V_{Zn} in AZO (3.2%)), and reported in each panel for sake of clarity and comparison. Vertical lines identify the position of the corresponding Fermi levels. Zero energy reference is set at the top of valence band of the ZnO host.

Atomic coordinates

AZO 3.2% (no defects)

Al -0.000126900 0.696678265 -0.004232680; Al 3.288375591 6.394394314 5.307722413; Zn 3.288374336 0.677340657 0.001587676; Zn -0.000125624 6.396577850 -0.000620525; Zn 3.288376056

6.383566792 -0.011637374; Zn -0.000126236 0.694965317 5.309306077; Zn 3.288374605 0.703843653 5.322036450; Zn -0.000125596 6.377974779 5.311583205; Zn 1.632530521 3.549281104 0.006198193; Zn 4.944220679 3.549280734 0.006198098; Zn 1.655070464 9.246452165 -0.002571059; Zn 4.921677957 9.246451805 -0.002570910; Zn 1.640044717 3.546707474 5.313478298; Zn 4.936706390 3.546706704 5.313478210; Zn 1.649915168 9.246598370 5.318033085; Zn 4.926836173 9.246599080 5.318033332; Zn -0.000126006 4.494000855 2.651881776; Zn 3.288375824 4.498425384 2.649834993; Zn -0.000126413 10.186167616 2.632664556; Zn 3.288374893 10.189422198 2.664456488; Zn -0.000125896 4.492479708 7.964389894; Zn 3.288375529 4.487208856 7.952200252; Zn -0.000125031 10.196450499 7.968235593; Zn 3.288376063 10.189064942 7.953671156; Zn 1.649636010 1.642056764 2.640709917; Zn 4.927113768 1.642056349 2.640710114; Zn 1.655613726 7.341171798 2.640716304; Zn 4.921137969 7.341171983 2.640717283; Zn 1.634178320 1.642914632 7.965584455; Zn 4.942572914 1.642914264 7.965584311; Zn 1.641178999 7.339742527 7.955547253; Zn 4.935572014 7.339742537 7.955546609; O -0.000126795 0.697555592 1.806762231; O 3.288374589 0.693636205 1.993342913; O -0.000125731 6.407787751 2.034922411; O 3.288376022 6.388170502 2.000786536; O -0.000125569 0.695320673 7.322188290; O 3.288375478 0.713950746 7.353357595; O -0.000125793 6.393548714 7.306290362; O 3.288375222 6.391112778 7.120230776; O 1.651071618 3.542012790 2.017563568; O 4.925679430 3.542012227 2.017563522; O 1.644075125 9.238154870 2.010356430; O 4.932674567 9.238154830 2.010356681; O 1.647386036 3.536543693 7.326358803; O 4.929364931 3.536543476 7.326358728; O 1.633998839 9.239380276 7.329651246; O 4.942753469 9.239380643 7.329651477; O -0.000126154 4.499426383 4.665354434; O 3.288375514 4.680421009 4.729314976; O -0.000125622 10.162897946 4.641298172; O 3.288375433 10.188020555 4.675993565; O -0.000125827 4.489615851 9.979029173; O 3.288375656 4.458136986 9.960833712; O -0.000127444 10.375397807 10.046233466; O 3.288374132 10.199267343 9.967242167; O 1.644597084 1.657293734 4.643690199; O 4.932152478 1.657292910 4.643690382; O 1.793978450 7.247037024 4.728915259; O 4.782773003 7.247037254 4.728916108; O 1.494889520 1.548323715 10.049204129; O 5.081859609 1.548323693 10.049203983; O 1.645978890 7.355508041 9.959150952; O 4.930772850 7.355508002 9.959150312.

AZO 3.2% ($\mathbf{V_O}$ close)

Al -0.000121717 0.700506578 -0.005232885; Al 3.288380568 6.484143027 5.341948463; Zn 3.288381902 0.674355728 0.005775474; Zn -0.000129047 6.387075735 -0.002530661; Zn 3.288375126 6.362366902 -0.002038188; Zn -0.000124035 0.710759657 5.295325262; Zn 3.288374329 0.707952685 5.310220943; Zn -0.000121200 6.336059272 5.328122100; Zn 1.635590355 3.557696189 0.013511150;

Zn 4.941194674 3.557689006 0.013518315; Zn 1.658942014 9.241621348 0.002030781; Zn 4.917807371 9.241623748 0.002031860; Zn 1.716305254 3.571333759 5.259875089; Zn 4.860462974 3.571324487 5.259879106; Zn 1.642626293 9.272763372 5.324726182; Zn 4.934142765 9.272765920 5.324720939; Zn -0.000123295 4.485860033 2.649738298; Zn 3.288376815 4.473136302 2.773932703; Zn -0.000128110 10.169832044 2.628081066; Zn 3.288371945 10.188380121 2.664269201; Zn -0.000127004 4.474186300 7.956517532; Zn 3.288376148 4.463397022 7.936386285; Zn -0.000125835 10.206515567 7.963086406; Zn 3.288376345 10.197476668 7.966106841; Zn 1.654829559 1.650060598 2.635649587; Zn 4.921919469 1.650056159 2.635650705; Zn 1.659356642 7.325037966 2.622410789; Zn 4.917384734 7.325036145 2.622409932; Zn 1.630885978 1.648348950 7.942800828; Zn 4.945861595 1.648348543 7.942801291; Zn 1.621864143 7.350274924 7.971948515; Zn 4.954881909 7.350278521 7.971948892; O -0.000133950 0.696968266 1.796485031; O 3.288368501 0.692844567 1.996529227; O -0.000134769 6.400511838 2.040663055; O 3.288365506 6.352012390 2.022762280; O -0.000132237 0.696851347 7.312553760; O 3.288369803 0.714643914 7.346698916; O -0.000134661 6.388020690 7.310481125; O 3.288366461 6.401196674 7.114065396; O 1.656074625 3.546356538 2.018666001; O 4.920676172 3.546353462 2.018672625; O 1.648286498 9.225174293 2.013865134; O 4.928448276 9.225173595 2.013867666; O 1.647598040 3.538133612 7.290781049; O 4.929143994 3.538133532 7.290780433; O 1.635075580 9.241903407 7.334298652; O 4.941669339 9.241905363 7.334294435; O -0.000128069 4.478423032 4.667419293; O -0.000115843 10.170396183 4.637735384; O 3.288378610 10.185812548 4.678016583; O -0.000116761 4.485918478 9.976954374; O 3.288398581 4.454006440 9.942066276; O -0.000134127 10.386331327 10.054179904; O 3.288370301 10.197918035 9.980430740; O 1.642001847 1.653942130 4.637922098; O 4.934736846 1.653937320 4.637923103; O 1.798163745 7.240660800 4.740482818; O 4.778601249 7.240659690 4.740487716; O 1.487324044 1.544669600 10.050064927; O 5.089438490 1.544670949 10.050062709; O 1.648241565 7.350417577 9.971038492; O 4.928494475 7.350420377 9.971037905.

AZO 3.2% (V_O far)

Al -0.000123676 0.696071267 -0.002589431; Al 3.288378436 6.393251648 5.309033497; Zn 3.288380166 0.668430405 0.006358425; Zn -0.000124281 6.397647109 -0.002416523; Zn 3.288377637 6.384323359 -0.013745237; Zn -0.000124108 0.691592619 5.304028057; Zn 3.288376314 0.703190750 5.316274027; Zn -0.000120046 6.366536621 5.318527173; Zn 1.632037010 3.553746624 0.007502595; Zn 4.944719992 3.553745095 0.007503234; Zn 1.658719387 9.242367527 -0.001015259; Zn 4.918034444 9.242368821 -0.001015904; Zn 1.631800653 3.545898132 5.314822153; Zn 4.944955253

3.545896704 5.314822671; Zn 1.653601099 9.250342769 5.320146167; Zn 4.923158237 9.250345157 5.320145192; Zn -0.000123931 4.495778461 2.650873833; Zn 3.288377686 4.503906666 2.642291851; Zn -0.000124469 10.175602402 2.631854803; Zn 3.288376515 10.188958918 2.663683339; Zn -0.000124328 4.492598950 7.971709610; Zn 3.288377115 4.478234722 7.948551642; Zn -0.000122866 10.200267983 7.958938600; Zn 3.288377959 10.190865233 7.959497477; Zn 1.654837170 1.648475424 2.639195465; Zn 4.921916887 1.648473627 2.639194923; Zn 1.656376310 7.338613033 2.634370822; Zn 4.920378563 7.338612906 2.634371006; Zn 1.632057529 1.642217507 7.955033588; Zn 4.944697017 1.642217353 7.955033728; Zn 1.633529744 7.344857588 7.952241346; Zn 4.943225734 7.344859193 7.952241526; O -0.000132248 0.697284298 1.798465841; O 3.288370457 0.694829600 1.994998561; O -0.000128740 6.407979701 2.035104967; O 3.288372485 6.390384314 2.001201780; O -0.000128798 0.695547266 7.319365478; O 3.288372285 0.713231462 7.352704758; O -0.000130119 6.391772991 7.307324945; O 3.288369685 6.392927158 7.110776503; O 1.652118288 3.545145346 2.017604545; O 1.644917297 9.235754831 2.010742903; O 4.931825533 9.235755058 2.010743860; O 1.644799876 3.537782850 7.326167721; O 4.931943611 3.537782289 7.326166817; O 1.634401143 9.241334605 7.330303157; O 4.942347451 9.241336411 7.330302564; O -0.000128918 4.500218713 4.666313087; O 3.288369199 4.690552742 4.734526097; O -0.000121719 10.159318886 4.642911492; O 3.288374435 10.187879366 4.676710682; O -0.000127988 4.490997782 9.986466317; O 3.288376424 4.458983768 9.959885592; O -0.000133035 10.385807822 10.050958930; O 3.288371210 10.196784358 9.975921734; O 1.643506608 1.658671516 4.645665268; O 4.933233545 1.658670739 4.645665399; O 1.802743287 7.241117009 4.736025015; O 4.774014410 7.241115070 4.736026671; O 1.485447653 1.543873290 10.054803402; O 5.091308459 1.543874994 10.054801778; O 1.645523151 7.354515413 9.958855625; O 4.931217977 7.354515960 9.958855060.

AZO 3.2% ($\mathbf{V}_{Zn}$)

Al -0.000113948 0.680969213 0.003985587; Al 3.288382425 6.392338524 5.370043230; Zn 3.288387179 0.666991442 0.019072220; Zn -0.000122122 6.396242239 0.011246184; Zn 3.288378645 6.366343437 -0.001265545; Zn -0.000129893 0.707349367 5.292095305; Zn 3.288372732 0.710792707 5.302764288; Zn -0.000116439 6.341056653 5.308514828; Zn 1.649622945 3.610458594 0.042869424; Zn 4.927130185 3.610457872 0.042870344; Zn 1.660668035 9.223889512 0.033730998; Zn 4.916095143 9.223892161 0.033728303; Zn 1.664107407 3.569524229 5.266127767; Zn 4.912644606 3.569523484 5.266127110; Zn 1.655823404 9.242055655 5.319842318; Zn 4.920926084 9.242056072 5.319843720; Zn -0.000139759 4.445451203 2.608521572; Zn -0.000123714 10.190115522

2.637070299; Zn 3.288378077 10.164678132 2.653823423; Zn -0.000123503 4.484010121 7.962479778; Zn 3.288377986 4.471160327 7.871484496; Zn -0.000123226 10.211030272 7.972317682; Zn 3.288375179 10.197465813 7.976615016; Zn 1.672710183 1.688974315 2.612174379; Zn 4.904042754 1.688972926 2.612170358; Zn 1.670787301 7.297952845 2.623749401; Zn 4.905960425 7.297954200 2.623748018; Zn 1.626943188 1.641171340 7.962143978; Zn 4.949807352 1.641172815 7.962143323; Zn 1.623300843 7.361548596 7.964471548; Zn 4.953453681 7.361550150 7.964472001; O -0.000137390 0.622267896 1.789913883; O 3.288367692 0.658421027 2.001494318; O -0.000131334 6.421221735 2.041454242; O 3.288371905 6.709513438 1.866890480; O -0.000132062 0.685312467 7.304486541; O 3.288370668 0.704578836 7.345093304; O -0.000129479 6.403565917 7.297431100; O 3.288372258 6.484542057 7.186206581; O 1.479817516 3.417044343 1.906577919; O 5.096885227 3.417056301 1.906585780; O 1.625651689 9.258085904 2.028851311; O 4.951101077 9.258086612 2.028846708; O 1.625373284 3.513318950 7.337545743; O 4.951378570 3.513319494 7.337544553; O 1.632550552 9.263143157 7.330648955; O 4.944196673 9.263144361 7.330651524; O -0.000128780 4.495441567 4.667864679; O 3.288375502 4.674119698 5.114801817; O -0.000132386 10.151327636 4.666534741; O 3.288370106 10.180931212 4.684419181; O -0.000132858 4.527358721 9.945042904; O 3.288369257 4.481225778 9.890428337; O -0.000106431 10.355845952 10.039075993; O 3.288378650 10.178657822 9.985210137; O 1.645479638 1.644067198 4.650318856; O 4.931254846 1.644066795 4.650317605; O 1.801103897 7.247026607 4.775901975; O 4.775661460 7.247026730 4.775902299; O 1.495528373 1.483850303 10.015647959; O 5.081249704 1.483853445 10.015648182; O 1.618631564 7.371351852 9.941412209; O 4.958129766 7.371353778 9.941412983.

AZO 3.2% ($\mathbf{V}_{Zn+O}$)

Al -0.002652434 0.670517258 -0.011897270; Al 3.285684715 6.394450169 5.323725074; Zn 3.327802175 0.708321655 0.002179444; Zn -0.012450394 6.357125012 -0.017124354; Zn 3.295137115 6.340709792 -0.033935845; Zn -0.008170878 0.706888602 5.297941813; Zn 3.291796680 0.720850466 5.316085788; Zn 0.001660041 6.348413565 5.326869276; Zn 1.611599432 3.620886627 -0.004295519; Zn 1.674648959 9.236361556 0.031155595; Zn 4.927854559 9.252134559 0.000644950; Zn 1.636221840 3.554727342 5.301322410; Zn 4.937456818 3.552625752 5.314103691; Zn 1.656768649 9.247142688 5.324876376; Zn 4.920606075 9.253089982 5.333481973; Zn -0.108294690 4.413883083 2.619601192; Zn 3.434626965 4.393044902 2.579331787; Zn -0.002133148 10.201461037 2.628650346; Zn 3.303329918 10.228913848 2.661868623; Zn -0.016593594 4.466657507 8.032751742; Zn 3.290434832 4.433295336 7.997256093; Zn 0.008029788 10.209543311 7.981507449;

Zn 3.287462751 10.208629657 7.990270684; Zn 1.643904412 1.673033822 2.610968669; Zn 4.872946935 1.928300500 2.606742527; Zn 1.663928996 7.282546450 2.621173437; Zn 4.915772687 7.316927375 2.627812046; Zn 1.626656483 1.647550321 7.966299536; Zn 4.950072122 1.654159460 8.017381936; Zn 1.631033642 7.328615473 7.991979521; O 0.002304106 0.703126434 1.800782600; O 3.314130232 0.736736666 2.013101194; O -0.014613867 6.377365991 2.062086146; O 3.307419875 6.341273095 2.017753110; O 0.012461836 0.678188074 7.297373874; O 3.277952448 0.706541881 7.337383297; O -0.006096787 6.414620629 7.293372443; O 3.290107661 6.435864966 7.116340336; O 1.645633564 3.565187745 2.034772571; O 1.656748528 9.224432766 2.059797011; O 4.933890060 9.232173071 2.028646091; O 1.636044935 3.507656013 7.285016150; O 4.929324544 3.521650494 7.302750778; O 1.638856652 9.244163806 7.330248458; O 4.944490633 9.253674634 7.339419711; O -0.000803055 4.504237940 4.665604259; O 3.283548816 4.695900009 4.775758026; O -0.001109014 10.150300800 4.647984109; O 3.289966931 10.188977237 4.681516994; O 0.126193871 4.603160750 9.919670693; O 3.099005902 4.598559292 9.870933831; O 0.047373894 10.321634403 10.076024327; O 3.286764944 10.179843755 9.996815355; O 1.640017803 1.650259253 4.628847308; O 4.931214904 1.654777831 4.656581896; O 1.799711197 7.248439811 4.738047193; O 4.773220176 7.254412106 4.743293265; O 1.494343537 1.507310281 10.043697240; O 5.077469134 1.252728405 9.940595112; O 1.640187993 7.404844990 9.979097725; O 4.930369695 7.384702785 9.966686165.

AZO 3.2% (H close)

Al -0.005638640 0.688735750 0.028896968; Al 3.223511144 6.557047243 5.363463827; Zn 3.269994360 0.666829782 0.035857720; Zn -0.027452826 6.412784941 0.030826241; Zn 3.262795173 6.424422191 -0.050062011; Zn 0.063457715 0.599132558 5.320300857; Zn 3.300825304 0.688044009 5.346288085; Zn -0.046763140 6.368244174 5.340916410; Zn 1.600209740 3.533506421 -0.020954069; Zn 4.935659603 3.543942655 -0.008671621; Zn 1.641530965 9.253021102 0.021831276; Zn 4.904460937 9.254296626 0.022005207; Zn 1.648863411 3.513843998 5.341237310; Zn 5.387274759 3.194713937 5.575515761; Zn 1.634878596 9.271465200 5.353143173; Zn 4.911394499 9.273461560 5.345933428; Zn -0.047870655 4.499724721 2.661044318; Zn 3.208646781 4.533899389 2.353236510; Zn -0.021663158 10.178230107 2.640588030; Zn 3.267659191 10.197697449 2.686011685; Zn 0.028019723 4.530614228 8.030124998; Zn 3.302072660 4.483950709 7.968884069; Zn -0.011442848 10.203738036 7.996136550; Zn 3.274229722 10.191151834 7.990924378; Zn 1.638544449 1.650892090 2.653179090; Zn 4.908694900 1.652582982 2.650008844; Zn 1.612294621 7.360916987 2.646843731; Zn 4.885928500 7.355224535 2.644722727; Zn 1.631694417 1.643391420 7.974074472; Zn

4.935660627 1.584521233 8.041473854; Zn 1.594580488 7.366567953 7.981842323; Zn 4.932000582 7.365235757 7.975965390; O -0.008640339 0.694097714 1.820988996; O 3.271558351 0.701571636 2.016784019; O -0.037203818 6.415981501 2.064085415; O 3.247113099 6.440533225 1.969614178; O 0.002036028 0.693347434 7.332977645; O 3.283584804 0.708375704 7.379998144; O -0.023686254 6.403310008 7.323850519; O 3.259711332 6.426093851 7.135743479; O 1.582966577 3.535863486 1.992466839; O 4.878243521 3.552947771 2.017250277; O 1.624421244 9.249284189 2.025532129; O 4.908810940 9.246571024 2.027429753; O 1.655010566 3.550330268 7.338611399; O 4.968295759 3.505961707 7.439083556; O 1.620224979 9.254523553 7.357709258; O 4.930841379 9.255633479 7.351274925; O -0.002326676 4.484279047 4.691534710; O 3.149704350 4.872356602 4.665635458; O -0.008237036 10.124640213 4.648220659; O 3.270638844 10.183382741 4.696182208; O -0.016677609 4.509960078 10.017693847; O 3.267410132 4.472549332 9.987798073; O -0.013724729 10.385682648 10.076488046; O 3.272956581 10.199050921 10.000234089; O 1.662844976 1.651034611 4.661141489; O 4.984771327 1.548787311 4.653342185; O 1.736163615 7.300759118 4.760613657; O 4.734451987 7.273051384 4.756522709; O 1.469884819 1.535486909 10.067964545; O 5.082965690 1.527290975 10.094225027; O 1.606918686 7.372721469 9.973786257; O 4.916992090 7.373481094 9.971440659; H 4.035923179 4.509411416 4.574622324.

AZO 3.2% (H far)

Al 0.010315052 0.680081424 -0.033129654; Al 3.282526659 6.414863971 5.322157869; Zn 3.265061191 0.661961407 -0.033810925; Zn -0.000764402 6.420320246 -0.014020577; Zn 3.293241775 6.398991485 -0.022985242; Zn 0.001279521 0.699728534 5.285346615; Zn 3.281314822 0.718603624 5.304129674; Zn -0.007145371 6.391177732 5.329977200; Zn 1.640765847 3.539114006 0.001760483; Zn 4.949679398 3.517192837 -0.191736537; Zn 1.656404959 9.240872701 -0.026622366; Zn 4.917363754 9.247277816 -0.015058180; Zn 1.623545112 3.546867329 5.328243464; Zn 4.938211782 3.576840614 5.418229192; Zn 1.651619760 9.264922715 5.320257703; Zn 4.919153992 9.263855260 5.315460111; Zn 0.138956270 4.622364574 2.671257352; Zn 3.203408929 4.590461722 2.683948927; Zn 0.011400871 10.133287840 2.628273129; Zn 3.264956824 10.152244595 2.657647379; Zn 0.019786204 4.518239804 7.983555787; Zn 3.266305323 4.506348695 7.952409112; Zn -0.001585507 10.203683144 7.938130836; Zn 3.287504945 10.193111589 7.945762806; Zn 1.651007299 1.653364893 2.637020567; Zn 4.925036646 1.312796681 2.624671715; Zn 1.665378288 7.371748532 2.645130469; Zn 4.917720946 7.359210910 2.643492513; Zn 1.629369418 1.644740673 7.936909803; Zn 4.940564349 1.619433927 7.932436061; Zn 1.633650347 7.360006122 7.949268085; Zn 4.940287711

7.359324537 7.949978194; O 0.014631926 0.664350958 1.766464462; O 3.242438505 0.653472204 1.956761531; O 0.008158080 6.458188023 2.023786691; O 3.287563089 6.416874242 1.993981681; O -0.002839455 0.699648906 7.293550385; O 3.284491465 0.714802429 7.332205667; O -0.001551628 6.403384328 7.313452007; O 3.285435756 6.407717718 7.117736360; O 1.663919739 3.554625824 2.015639122; O 4.940481054 3.558521425 2.306530699; O 1.641366290 9.231088411 1.984930174; O 4.925843904 9.245185697 1.998096633; O 1.640437722 3.546658489 7.331381704; O 4.931582460 3.547151861 7.389871465; O 1.634081508 9.249467711 7.322149973; O 4.940066713 9.248985609 7.320079251; O -0.012919276 4.511923110 4.673803806; O 3.278077866 4.708588753 4.758366134; O -0.002708519 10.165005433 4.631083182; O 3.285658326 10.201795956 4.665769345; O 0.004636489 4.495166294 10.011288140; O 3.296443511 4.459746827 9.977707035; O 0.000897210 10.380306270 10.020081135; O 3.286649871 10.191378811 9.955344756; O 1.639718590 1.670162717 4.633041643; O 4.933346918 1.702143704 4.589233487; O 1.799988969 7.253983812 4.736633933; O 4.766371286 7.253037293 4.737800655; O 1.478731282 1.543480819 10.029779489; O 5.094033372 1.536920941 10.055144534; O 1.648799046 7.355649531 9.947040078; O 4.932198396 7.361913767 9.949253283; H 5.038646819 3.274816173 3.226356005.

AZO 3.2% ($\mathbf{V}_{Zn} + H$)

Al 0.011343097 0.680858612 0.016731348; Al 3.308920410 6.373748894 5.367415100; Zn 3.288792530 0.652816237 0.021761262; Zn 0.013188343 6.400128836 0.019838749; Zn 3.302133907 6.371578771 0.014455094; Zn 0.025489363 0.687803424 5.309121750; Zn 3.310318612 0.695221050 5.321694956; Zn 0.019524261 6.354454140 5.327725870; Zn 1.651597792 3.562773404 0.022628336; Zn 4.956712596 3.555856131 -0.088705585; Zn 1.667753348 9.223430564 0.029026439; Zn 4.926178274 9.220888239 0.031166616; Zn 1.690016334 3.555776637 5.302237175; Zn 4.946927190 3.559811374 5.329829554; Zn 1.672864327 9.232191388 5.330267405; Zn 4.937918806 9.232760157 5.333179990; Zn 0.114237705 4.519234549 2.673302383; Zn 0.014737493 10.154793214 2.651866328; Zn 3.302066278 10.158639573 2.670690281; Zn 0.027805057 4.494176061 7.975054631; Zn 3.296796226 4.483226693 7.896678767; Zn 0.004317207 10.201155774 7.977880381; Zn 3.294634756 10.185976539 7.978861158; Zn 1.672838507 1.653539304 2.650107127; Zn 4.941391525 1.595293680 2.655275557; Zn 1.720378348 7.295250529 2.638822231; Zn 4.920904360 7.302708065 2.646726877; Zn 1.643724325 1.632059151 7.966055295; Zn 4.961070563 1.629114712 7.958447581; Zn 1.640240749 7.358164088 7.974346147; Zn 4.962344493 7.353082747 7.971880400; O 0.022940966 4.489723914 4.673633905; O -0.027338291 0.653002118 1.813070147; O 3.302447456 0.676007995

2.009750532; O 0.027353821 6.409193021 2.055493823; O 3.325663506 6.564540706 1.922770896; O 0.010943519 0.686535908 7.320302195; O 3.306476774 0.704433671 7.357640208; O 0.015775216 6.394176301 7.314532831; O 3.299675240 6.454142174 7.184273465; O 1.429882727 3.383245038 1.909486809; O 4.918199907 3.529923031 1.969869132; O 1.649835298 9.241127566 2.029633521; O 4.957787349 9.240735418 2.031533499; O 1.645186538 3.514857186 7.353797010; O 4.967617216 3.518279404 7.374692759; O 1.638576327 9.253138009 7.340812426; O 4.950753188 9.249936865 7.342242705; O 3.321205166 4.654398830 5.066076370; O 0.016868587 10.147732695 4.666508876; O 3.307407058 10.178002731 4.688128299; O 0.007033161 4.508171748 9.977061375; O 3.297495029 4.452535157 9.927308144; O 0.004495816 10.371361755 10.061075877; O 3.299818884 10.180450500 9.992716369; O 1.668054541 1.642285041 4.662091498; O 4.958941867 1.653818411 4.646270767; O 1.824804799 7.228610873 4.770933142; O 4.794131982 7.231211398 4.776998897; O 1.500986641 1.495573063 10.043120132; O 5.101120126 1.538004841 10.069595522; O 1.641821322 7.357222685 9.962539388; O 4.964003107 7.356843341 9.958734939; H 4.127292765 4.011839597 2.238108348.

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