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## Comment on 'Nanoscale mapping of optical band gaps using monochromated electron energy loss spectroscopy' by Zhan, Granerød, Venkatachalapathy, Johansen, Jensen, Kuznetsov and Prytz in *Nanotechnology* 28 (2017) 105703

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7 Comment on 'Nanoscale mapping of optical band gaps using monochromated electron  
8 energy loss spectroscopy' by Zhan, Granerød, Venkatachalapathy, Johansen, Jensen,  
9 Kuznetsov and Prytz in *Nanotechnology* **28** (2017) 105703  
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12 In the above article [1] the authors attempt to measure the band gap of pure and of cadmium  
13 enriched zinc oxide from low-energy or valence electron energy-loss spectroscopy (VEELS)  
14 in a monochromated and aberration corrected scanning transmission electron microscope  
15 (STEM) and claim a 'spectral precision of 20meV'. As this is a factor of 7.5 better than the  
16 quoted energy resolution of their spectrometer of 0.15eV, this would be very impressive, and  
17 for investigating doping effects such a precision would be highly desirable. It is clear that the  
18 precision can be better than the resolution by several factors if the sampling is sufficiently  
19 fine, however, there are a few problems with the data that make this claim appear  
20 questionable. The whole situation is complicated by the fact that the manuscript shows only  
21 processed but no raw data and that essential experimental variables, such as convergence and  
22 collection angles, as well as relevant fitting parameters, such as begin and end positions of  
23 the fit range and  $R^2$  values of the fits, are not provided. These points could have been picked  
24 up by a careful reviewer.  
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30 The authors have basically applied a standard approach of subtracting an exponential  
31 extrapolation of the zero loss peak and fitting a square root function to a 3.5eV wide spectral  
32 range of the remainder. From the standard deviation of 0.02eV of their data when repeating  
33 the same experiment at various points in the same specimen they conclude this to be the  
34 'precision' of their experiment and add corresponding error bars to their plot. With  
35 comparison to cathodoluminescence data they then claim 'both excellent accuracy and  
36 precision'.  
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40 Unfortunately, data interpretation is not easy and may not be so straightforward with VEELS.  
41 In the following, some aspects related to methodology, statistics and physics are considered.  
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44 Firstly, other methods of zero loss peak removal (deconvolution [2,3], mirroring the peak  
45 tails and subtraction, which works well for a monochromator where the zero loss peak should  
46 be symmetrical [4,5], different multi-exponential fittings as reviewed in [6], together with  
47 Cerenkov effects) could (and will) produce different numerical values for the band gap. The  
48 authors admit that 'the exact fit range of the background model influences the extracted band  
49 gap value', however, to what degree other methods of zero loss peak removal or other fitting  
50 ranges would influence the results seems to not have been explored. The statement that 'for  
51 the most accurate results, this fitting region should be chosen close to the expected onset of  
52 the band gap transitions being studied' is certainly correct but close to a tautology and  
53 perhaps not particularly helpful: this seems to imply that they can only measure the band gap  
54 precisely if they know it beforehand and so know where to place the fitting range! It means  
55 that the procedure described may, at the best work, for zinc oxide under the given (unknown)  
56 conditions of data acquisition and processing but is likely to fail for any other semiconductor  
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and will probably not be able to predict unknown band gaps for methodological reasons. The general title of the publication, however, would have seemed to imply to readers a fairly widespread validity.

Secondly, the small spectral sections shown in the inset of one figure (Figure 4) depict a strong rise of absorption near the suspected band gap of  $\sim 3\text{eV}$  but are then followed by a plateau from  $\sim 3.5$  to  $5\text{eV}$ , so the net signal does clearly NOT increase like a square root function. We have recently reported this for InGaN and pointed out that including an offset will alter but not improve the fit quality [7]. Hence, fitting such a function, of which no details are given, will not be very good (in terms of fit quality) and probably not be particularly reliable (in terms of reproducibility). It would be nice had the authors at least stated the  $R^2$  values obtained, better still, explored the variation of  $R^2$  values with extension and positioning of the fitting range [8]. This may have produced a much larger statistical error than the  $20\text{meV}$  stated, and it appears questionable whether a small scatter obtained by repeatedly applying their method to spectra extracted from pure zinc oxide from adjacent regions would also be useful to characterize the general precision of a technique that may significantly deteriorate in the case of small thickness, orientational and/or compositional variations within the specimen.

Thirdly, VEELS always shows strong plasmon peaks (for zinc oxide at  $18.8\text{eV}$  [9], for zinc at  $17.2\text{eV}$  [10]) the long tail components of which have been shown to also influence the numerical fitting results [7]. Moreover, for the specific materials system of zinc oxide under consideration here there are further, weaker valence interband transitions at  $3.8$ ,  $5.5$ .,  $9.5$  and  $13.5\text{eV}$  [9], and there may be a pronounced surface plasmon peak around  $15.8\text{eV}$  [11] in a thin foil sample, so fitting a simple square-root function to a small range which will inevitably contain several weak humps and shoulders makes physically rather limited sense. The underlying fundamental reason is that the free-electron approximation for a three-dimensional perfect bulk material implicitly assumed in the derivation of the square-root function for the density of states is not necessarily fulfilled in this crystalline material.

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