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Comment on "Characteristics of Multi-photon Absorption in a β-Ga_2O_3 Single Crystal" [J. Phys. Soc. Jpn. 88, 113701 (2019)]

Rafał Korlacki[1]*, Alyssa Mock[2], Chad Briley[1], Vanya Darakchieva[3], Bo Monemar[3,4], Yoshinao Kumagai[5,4], Ken Goto[5,6], Masataka Higashiwaki[7], and Mathias Schubert[1,3,8]

[1]*Department of Electrical and Computer Engineering, University of Nebraska-Lincoln, Lincoln, NB 68588, U.S.A.*
[2]*National Research Council Postdoctoral Fellow, residing at U.S. Naval Research Laboratory, Washington, DC 20375, U.S.A.*
[3]*Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE 58183, Linköping, Sweden*
[4]*Global Innovation Research, Tokyo University of Agriculture and Technology, Koganei, Tokyo 183-8538, Japan*
[5]*Department of Applied Chemistry, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan*
[6]*Tamura Corporation, Sayama, Saitama 350-1328, Japan*
[7]*National Institute of Information and Communications Technology, Koganei, Tokyo 184-8795, Japan*
[8]*Leibniz Institute for Polymer Research, Dresden, D-01005, Germany*

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Most recently, Yamaoka, Mikuni, and Nakayama[1)] investigated a range of multi-photon absorption processes in a single crystal of monoclinic β-Ga_2O_3. They observed 2-, 3-, 4-, and 5-photon processes, and speculated that the 5-photon absorption corresponding to the transition energies above 7 eV may involve transitions at various high-symmetry points outside of the Brillouin-zone center. In this comment we provide evidence from computational analysis, based on the results of first-principles calculations, supporting the hypothesis about the origin of the 5-photon absorption process in monoclinic β-Ga_2O_3. The possibility of selective excitation of optical transitions at high-symmetry points away from the Brillouin-zone center is an attractive prospect for future detailed studies of the band structure of this important material. Specifically, Yamaoka, Mikuni, and Nakayama identified four such points (Y, Z, L, and F) in the band structure obtained from first-principles calculations, including, among others, one that was presented in our recent paper[2)] (Ref. 16 in 1). For this comparison, however, Yamaoka, Mikuni, and Nakayama only considered the lowest possible transition energies at the respective high-symmetry points, i.e., the energy gaps between the highest occupied and lowest unoccupied bands at these points, as read from the plots of the band structure.

Fortunately, three of the four high-symmetry points identified by Yamaoka, Mikuni, and Nakayama as possible candidates for optical transitions away from the Γ-point are included in the regular grid used in our density functional theory (DFT) calculations, from which we reported band structure results and Γ-point transition matrix elements in our previous work.[2)] Hence, we are able to extract information on the matrix elements $|\mathcal{M}_{cv}|^2$ of the momentum operator between conduction and valence bands for these three points. Regardless of subtleties of selection rules for single- and multi-photon absorption processes, non-trivial values of these matrix elements indicate a wavefunction overlap between the initial and the final states involved in the transition. Hence, small and vanishing values rule out transitions, which should occur only with very small transition strength, or which cannot occur at all. Thus, we are able to immediately test the hypothesis put forward by Yamaoka, Mikuni, and Nakayama. Furthermore, our analysis need not to be limited to just the lowest gap energy, but we can identify all relevant band pairs that may participate in optical transitions in any particular energy range. In fact, for two of the three high-symmetry points we will discuss, the band-edge transition is not allowed regardless of polarization direction. It is worth noting that in our original paper (Ref. 2) we only presented DFT-derived transition matrix elements for the Brillouin-zone center, as we could see no evidence of possible band-to-band transitions originating at locations within the band structure other than the Γ-point in spectroscopic ellipsometry results.

Here, we present two tables with matrix elements separately for the monoclinic **a**–**c** plane and for the symmetry axis **b**, analogous to Tables V and VI in our previous paper (Ref. 2), for three high symmetry points: Y, Z, and L, as defined in Table I and Fig. 2 of Ref. 2. We include values for all directions within the crystal of β-Ga_2O_3, in a Cartesian coordinate system aligned with the crystallographic vectors **a**, **b**, and $\mathbf{c}^\star$, as defined in Fig. 1 of Ref. 2, and for transition energies up to 10 eV, which is a reasonable energy limit accessible in optical experiments. All transitions are labelled Ξ_{c-v}, where Ξ = Y, Z, or L, and c and v are indices of the bands counted from the band gap, i.e., the lowest energy transition between the highest valence band ($v = 1$) and the lowest conduction band ($c = 1$) is labelled "1-1". The transitions listed in Tables I and II is a complete list of all transitions in the energy range below 10 eV, for which the matrix elements are non-negligible, i.e., which exceed the threshold of 5×10^{-9} $(\hbar/\mathrm{Bohr})^2$.

The multi-photon absorption experiments by Yamaoka, Mikuni, and Nakayama were performed with the excitation laser polarized along the crystallographic direction **c** ($\alpha \approx 103°$). As can be read from our tables presented here, there is a number of band-to-band transitions polarized close enough to the laser beam that they are available for optical excitation in the investigated energy range of 5-photon absorption (≈ 7.2–7.8 eV). Even the transitions at the point Z, all of which below 9 eV are polarized very close to the crystallographic direction **a**, may still be partially excited. Additionally, if we take into account that all DFT-calculated energies presented here are likely slightly lower than the actual energies (which is indicated, for example, by 0.3 eV difference between the lowest calculated transition Γ_{1-1} and the lowest transition measured by ellipsometry[2)]) it is possible that the Y_{1-1} transition also contributes to the 5-photon process. It is worth noting that multi-photon

Table I. Calculated band-to-band transition energies (E) within the **a**–**c** plane, and transition matrix elements $|\mathcal{M}_{cv}|^2_a$ and $|\mathcal{M}_{cv}|^2_{c^\star}$ projected onto directions **a** and **c***, respectively, in atomic units $(\hbar/\mathrm{Bohr})^2$. Transitions are labelled Ξ_{c-v}, where Ξ = Y, Z, or L with indices numbering bands upwards from the bottom ($c = 1$) of the conduction band and downwards from the top ($v = 1$) of the valence band at the respective high-symmetry points. The polarization angle α is measured relative to axis **a**.

Label	E (eV)	α(°)	$\lvert\mathcal{M}_{cv}\rvert^2_a$	$\lvert\mathcal{M}_{cv}\rvert^2_{c^\star}$	c	v
Y, 1-1 gap energy 6.917 eV						
Y_{1-1}	6.917	93.5	0.00351038	0.05739823	1	1
Y_{2-2}	7.430	78.8	0.00050898	0.00257305	2	2
Y_{1-5}	7.788	123.3	0.00394674	0.00601592	1	5
Y_{2-6}	8.191	92.8	0.00782950	0.16143283	2	6
Y_{3-1}	8.263	102.3	0.00163581	0.00749671	3	1
Y_{1-11}	8.927	89.1	0.00030399	0.01924516	1	11
Y_{2-9}	9.043	0.9	0.01403287	0.00023117	2	9
Y_{3-5}	9.135	85.6	0.00156774	0.02035981	3	5
Y_{4-2}	9.283	161.8	0.06746660	0.02217919	4	2
Y_{1-13}	9.460	94.4	0.00729752	0.09533864	1	13
Y_{2-12}	9.479	85.6	0.00064415	0.00841221	2	12
Z, 1-1 gap energy 7.285 eV						
Z_{2-1}	7.439	179.9	0.08093236	0.00014469	2	1
Z_{1-4}	7.469	177.0	0.04754691	0.00252405	1	4
Z_{2-5}	7.744	3.5	0.00972378	0.00060113	2	5
Z_{1-7}	8.523	179.9	0.12575050	0.00028210	1	7
Z_{1-10}	9.101	121.8	0.00026706	0.00043097	1	10
Z_{2-8}	9.133	172.0	0.01191995	0.00168371	2	8
Z_{3-4}	9.518	80.3	0.00323620	0.01889754	3	4
Z_{1-13}	9.583	88.5	0.00002734	0.00106447	1	13
Z_{4-1}	9.720	74.1	0.00082672	0.00290836	4	1
L, 1-1 gap energy 7.373 eV						
L_{2-1}	7.621	76.2	0.01046947	0.04254467	2	1
L_{1-2}	7.960	61.2	0.04814896	0.08750955	1	2
L_{1-4}	8.116	179.9	0.02560934	0.00002250	1	4
L_{2-9}	8.581	89.3	0.00004246	0.00351413	2	9
L_{4-1}	8.684	172.2	0.01800037	0.00245251	4	1
L_{3-2}	9.143	8.9	0.02876275	0.00452457	3	2
L_{3-4}	9.299	152.7	0.06351346	0.03283526	3	4
L_{5-1}	9.313	178.6	0.02163426	0.00053012	5	1
L_{4-9}	9.643	139.8	0.00393155	0.00331980	4	9
L_{2-6}	9.907	31.3	0.06060765	0.03686868	2	6

absorption is a non-linear process, and high intensity light sources are used for measurements. Therefore, even transitions with relatively low probabilities cannot be neglected.

In summary, we have provided evidence, based on the results of first-principles calculations, that the hypothesis about the origin of the 5-photon absorption process observed by Yamaoka, Mikuni, and Nakayama[1] is indeed entirely plausible. The possibility of selective excitation of optical transitions at high-symmetry points away from the Brillouin-zone center, something that Yamaoka, Mikuni, and Nakayama also postulate, is an attractive prospect for future detailed studies of the band structure of this emerging and important material.

Table II. Same as Table I for polarization parallel to the crystallographic direction **b**.

Label	E (eV)	$\lvert\mathcal{M}_{cv}\rvert^2$	c	v
Y, 1-1 gap energy 6.917 eV				
Y_{1-4}	7.382	0.01353799	1	4
Y_{2-3}	7.698	0.00611077	2	3
Y_{1-8}	8.257	0.09823719	1	8
Y_{2-7}	8.442	0.12323332	2	7
Y_{3-4}	8.729	0.00595599	3	4
Y_{2-10}	9.064	0.00338082	2	10
Y_{4-3}	9.551	0.03015652	4	3
Y_{3-8}	9.603	0.04667987	3	8
Y_{1-14}	9.901	0.01895232	1	14
Z, 1-1 gap energy 7.285 eV				
Z_{2-2}	7.791	0.12273567	2	2
Z_{1-3}	8.446	0.12756554	1	3
Z_{1-6}	8.472	0.05435033	1	6
Z_{2-9}	9.228	0.06261109	2	9
Z_{2-12}	9.527	0.00232840	2	12
Z_{1-11}	9.658	0.02659316	1	11
L, 1-1 gap energy 7.373 eV				
L_{1-5}	8.072	0.02708365	1	5
L_{2-3}	8.247	0.10259964	2	3
L_{1-7}	8.550	0.19919557	1	7
L_{3-5}	9.255	0.10605254	3	5
L_{4-3}	9.309	0.01480395	4	3
L_{2-8}	9.498	0.05404957	2	8
L_{3-7}	9.733	0.03840487	3	7
L_{1-10}	9.907	0.00198014	1	10
L_{5-3}	9.938	0.05284500	5	3

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*rkorlacki2@unl.edu

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