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Origin of green luminescence in hydrothermally grown ZnO single crystals

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Combining photoluminescence and positron annihilation studies of hydrothermally grown ZnO crystals with stoichiometry varied by controlled annealing enabled us to clarify the origin of green luminescence. It was found that green luminescence in ZnO has multiple origins and consists of a band at 2.3(1) eV due to recombination of electrons of the conduction band by zinc vacancy acceptors coupled with hydrogen and a band at 2.47(2) eV related to oxygen vacancies. The as-grown ZnO crystals contain zinc vacancies associated with hydrogen and exhibit a green luminescence at 2.3(1) eV. Annealing in Zn vapor removed zinc vacancies and introduced oxygen vacancies. This led to disappearance of the green luminescence band at 2.3(1) eV and appearance of a green emission at higher energy of 2.47(2) eV. Moreover, the color of the crystal was changed from colorless to dark red. In contrast, annealing of the as-grown crystal in Cd vapor did not remove zinc vacancies and did not cause any significant change of green luminescence nor change in coloration. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4922944]

Zinc oxide (ZnO) is a wide band gap (3.37 eV at room temperature) semiconductor with a high exciton binding energy of 60 meV.[1] Because of these properties, ZnO attracts great attention as a material suitable for UV light emitting diodes and lasers. Photoluminescence spectrum of ZnO typically consists of a UV near band edge emission and a broad deep band emission around 500–580 nm (2.5–2.1 eV) called "green luminescence" (GL).[1] It is known that GL is related to point defects, but the nature of these defects remained controversial for a long time.[1] A variety of point defects including oxygen vacancies (V_O),[2] zinc vacancies (V_{Zn}),[3,4] zinc interstitials (Zn_i),[5] as well as zinc antisites[6] have been proposed as candidates for GL centers. *Ab-initio* theoretical calculations[3] revealed that V_O and V_{Zn} should be dominating defects in ZnO prepared under Zn-rich and O-rich conditions, respectively.

Leiter *et al.*[2] attributed the GL band at 2.45 eV to V_O. Under UV irradiation, a neutral V_O containing two electrons passes to an excited singlet state and then relaxes to an excited triplet state, from which the center luminescences. Guo *et al.*[4] assigned GL to electronic transitions from the conduction band (CB) to V_{Zn} acceptor level in the band gap. The calculated position of the V_{Zn} level ~0.8 eV above the valence band (VB)[3] is consistent with GL at the wavelength around 500 nm. Recent study of ZnO powders annealed in oxidizing and reducing atmospheres revealed GL at ~2.3 and ~2.5 eV, and these emissions were assigned to V_{Zn} and V_O, respectively.[7]

Positron annihilation spectroscopy (PAS)[8] provides an opportunity to identify unambiguously V_{Zn} but is insensitive to V_O. This is caused by the fact that V_{Zn} represents a deep positron trap while V_O is incapable of positron localization.[9,10] In the present work, photoluminescence (PL) studies of ZnO single crystals with various stoichiometry were combined with PAS characterizations to link changes in GL with the development of vacancies.

Commercially available ZnO single crystals are most frequently prepared by the hydrothermal growth technique.[11] Hydrothermally grown (0001) ZnO single crystals studied in this work were supplied by the MaTecK GmbH (Jülich, Germany). The ZnO crystals with polished O-terminated faces were studied (i) in the as-grown state, (ii) after annealing in Zn vapor, and (iii) after annealing in Cd vapor. The annealing was performed by sealing ZnO crystal into an evacuated quartz ampoule together with Zn (or Cd) metal and annealing the ampoule in a furnace at 1000 °C for 12 h.

A digital positron lifetime (LT) spectrometer[12] with time resolution of 145 ps was employed for PAS investigations. A ^{22}Na positron source with activity of 1.1(2) Mq was deposited on a 2 μm Mylar foil and sealed between two pieces of ZnO crystals studied. At least 10^7 annihilation events were collected in each LT spectrum. Source contribution consisting of two components with lifetimes of 368(2) ps and 1.52(5) ns and corresponding intensities of 8.4(2) % and 1.2(1) % has been always subtracted from the spectra. Decomposition of LT spectra was performed using a maximum likelihood procedure.[13] The quality of fit was checked by the $\chi 2$ test. For all fits considered here, the $\chi 2$ values divided by the number of degrees of freedom fell into the range 1.00–1.02.

Steady state PL spectra were excited either by light-emitting diodes or a Xe lamp connected to a 15-cm monochromator, which enabled to measure PL excitation (PLE) spectra. Emitted PL was dispersed by another 15-cm monochromator

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and detected by a photomultiplier. All PL spectra are corrected for the spectrometer response. Both PAS and PL studies were carried out at room temperature.

The PL spectra of ZnO crystals excited by the wavelength of 325 nm are plotted in Fig. 1(a). The PL spectrum of the as-grown ZnO crystal consists of a UV excitonic peak at 3.29(1) eV and a broad GL band centered around 2.3 eV. The GL emission can be well described by superposition of two Gaussian contributions, see solid line in Fig. 1(a). Their parameters are listed in Table I. As was suggested by Børseth *et al.*,[14] the shorter wavelength component at the energy 2.08–2.18 eV probably corresponds to the yellow luminescence band assigned to Li impurities which are common in hydrothermally grown ZnO crystals. Indeed, chemical analysis by inductively coupled plasma mass spectrometry revealed that ZnO crystals studied contain Li impurities with concentration falling in the range $(1-3)\times10^{16}\,\mathrm{cm}^{-3}$. The Li concentration was found to be virtually unchanged after annealing. The longer wavelength component located at the energy of 2.3(1) eV agrees well with the emission attributed to V_{Zn} related centers.[7,14] PAS studies revealed that the as-grown ZnO crystal exhibits a single component LT spectrum with lifetime of 181.1(5) ps, see Table I. This lifetime is typical for hydrothermally grown ZnO crystals[9,15] and agrees well with the lifetime calculated for V_{Zn} associated with hydrogen ($V_{Zn}+H$).[10] Hence, hydrothermally grown ZnO crystal contains $V_{Zn}+H$ complexes in the as-grown state with concentration at least 10^{18} cm^{-3} leading to saturated positron trapping. The GL band at 2.3(1) eV is, thereby, caused by transition from CB to the $V_{Zn}+H$ acceptor level in the band gap.

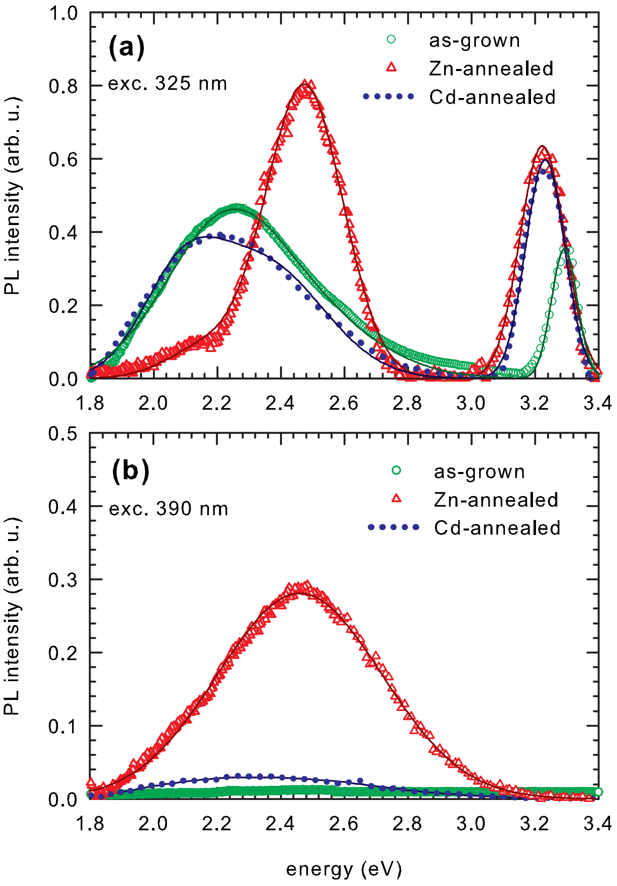

FIG. 1. PL spectra of ZnO crystals in the as-grown state and after annealing in Zn and Cd vapor: (a) excitation using wavelength of 325 nm, (b) excitation using wavelength of 390 nm. Solid lines represent fits by Gaussian emission bands.

TABLE I. Results of PAS studies: the positron lifetime τ obtained from decomposition of LT spectra; results of PL measurements with excitation wavelength of 325 nm: decomposition of GL in Fig. 1(a) into two Gaussian contributions with maxims at energies E_i and relative intensities I_i. The width of the Gaussian contributions falls into the range 0.15–0.25 eV. Standard deviations are given in parentheses in the units of the last significant digit.

	PAS	PL excitation 325 nm			
Sample	τ (ps)	I_1	E_1 (eV)	I_2	E_2 (eV)
as-grown	181.1(5)	60(10)	2.18(9)	40(10)	2.31(9)
Zn-annealed	166.2(5)	20(2)	2.17(2)	80(2)	2.47(2)
Cd-annealed	180.4(5)	57(5)	2.08(7)	43(5)	2.3(1)

One can see in Fig. 1(a) that annealing in Zn vapor led to a blue shift of the defect related emission. The emission associated with $V_{Zn}+H$ disappeared, and the GL band of the Zn-annealed crystal consists of the Li related yellow luminescence at 2.17(2) eV and a new dominating emission band at 2.47(2) eV, see Table I. Moreover, PAS investigations showed that positron lifetime decreased from 181.1(5) down to 166.2(5) ps, which is close to the lifetime measured in vapor phase and pressurized melt grown ZnO crystals.[16,17] Note that the bulk positron lifetime for a perfect ZnO lattice obtained from *ab-inito* theoretical calculations is 154 ps.[10] Hence, there are two possible interpretations: (i) the lifetime measured in the Zn-annealed sample comes from free positrons, i.e., the actual bulk ZnO lifetime is around 166 ps as suggested by Tuomisto *et al.*;[16] (ii) the lifetime of 166 ps corresponds to some other defects with open volume smaller than $V_{Zn}+H$ complexes, e.g., stacking faults proposed by Anwand *et al.*[17] Nevertheless, in both cases, the present result testifies that by annealing in Zn vapor, $V_{Zn}+H$ complexes were removed from the sample. It has been demonstrated that Zn-annealing led to introduction of V_O.[18–21] Hence, the new emission band at 2.47(2) eV in the Zn-annealed crystal could be attributed to V_O centers. Since V_O do not trap positrons[10] they cannot be detected directly by PAS. But, it has been shown[22] that when a sample containing V_{Zn} and V_O is annealed at 500 °C, presence of V_O is revealed through formation of clusters of V_O merged with V_{Zn}. The Zn-annealed crystal was extensively ground using a SiC 120 paper in order to roughen the surface and to introduce V_{Zn} into a sub-surface region. Subsequently, the sample was annealed at 500 °C in air. The LT spectrum of the annealed sample consists of two components with lifetimes $\tau_1 = 167(1)$ ps, $\tau_2 = 440(9)$ ps, and intensities $I_1 = 91(1)$ %, $I_2 = 9(1)$ %. The second component represents a contribution of positrons trapped at clusters formed by agglomeration of V_O which became mobile during annealing and merged with V_{Zn} in the sub-surface region. Hence, the annealing experiment confirmed existence of V_O in the Zn-annealed crystal.

Annealing in Zn vapor changed the color of the ZnO crystal from colorless to dark red as shown in Fig. 2. In

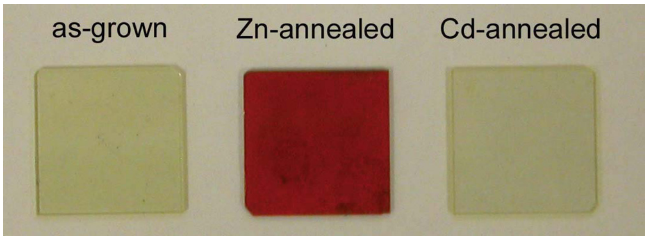

FIG. 2. Photographs of ZnO crystals in the as-grown state and after annealing in Zn and Cd vapor.

contrast, annealing in Cd vapor did not change color of the as-grown crystal and also the positron lifetime remained practically the same as in the as-grown sample testifying that $V_{Zn} + H$ were not removed by Cd-annealing. Fig. 1(a) shows that GL of the Cd-annealed crystal is very similar to that in the as-grown sample.

The optical transmittance of ZnO crystals is plotted in Fig. 3. The as-grown crystal and the crystal annealed in Cd vapor exhibit similar transmittance curves characterized by a sharp absorption edge at $\sim$3.2 eV. For the Zn-annealed crystal, the absorption edge shifted down to $\sim$2.4 eV. Similar shift has been reported[19] for a ZnO crystal grown by seeded chemical vapor and annealed in Zn vapor in similar way as in the present work.

Note that the UV emission peak in Fig. 1(a) was enhanced in the annealed samples. This is most probably due to improvement of crystal perfection mainly by recovery of dislocations introduced into the virgin crystal by surface polishing.[9] The observed shift of the maximum of the UV emission to lower energy is likely related to shallow donors which were introduced by annealing and will be discussed in the following text.

The PLE spectra detected at 550 nm (2.25 eV) are plotted in Fig. 4. The as-grown and Cd-annealed crystals exhibit very similar PLE spectra characterized by a sharp edge at the bang gap energy of 3.37 eV. In contrast, the PLE curve for the Zn-annealed crystal contains a pronounced resonance peak in the below-band-gap region at 3.2 eV testifying that there is a remarkable GL excitation involving states inside the band gap. The PL spectra collected using an excitation of 390 nm (3.18 eV) are shown in Fig. 1(b). While GL disappeared in the virgin and Cd-annealed sample, the Zn-annealed crystal exhibits green emission which is well described by a Gaussian GL band centered at 2.46(2) eV, see the solid line in the figure.

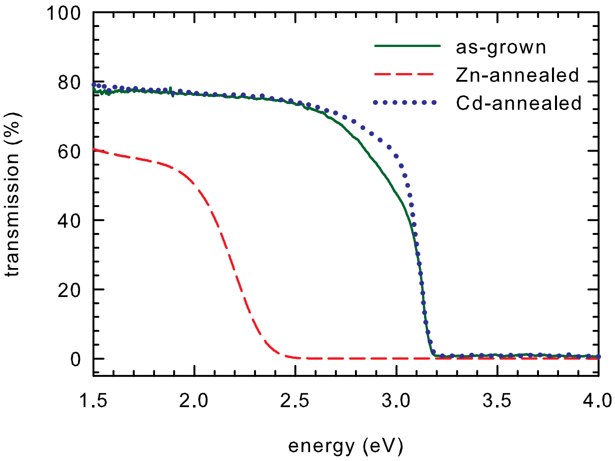

FIG. 3. The transmittance of ZnO crystals in the as-grown state and after annealing in Zn and Cd vapor.

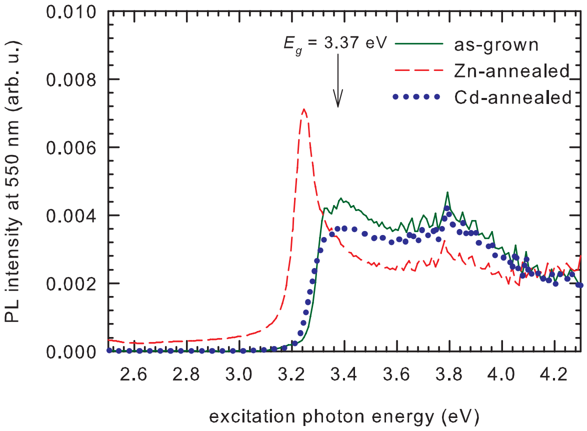

FIG. 4. PLE spectra of ZnO crystals in the as-grown state and after annealing in Zn and Cd vapor. The spectra were detected at 550 nm. The arrow indicates the band gap energy.

Several models for room temperature GL associated with V_O centers can be considered. One possibility shown in Fig. 5(a) assumes recombination of electrons photoexcited to CB or shallow donor levels with holes at V_O level. The triplet-to-singlet state model[2] shown in Fig. 5(b) involves photoexcitation of V_O center from the singlet to the triplet state and subsequent radiation recombination of the triplet state. Kodama and Uchino[23] extended the triplet-to-singlet state model and proposed that in addition to the direct emission process, a thermally assisted indirect emission takes place and dominates when the excitation energy comes near or below the band gap energy. The indirect emission illustrated in Fig. 5(c) involves both V_O and shallow donors and is realized by the following sequence:[23] (i) thermally induced ionization of shallow donors; (ii) photo induced electron transfer from V_O to the empty donor levels; (iii) electron capture by ionized V_O and formation of the triplet V_O center; and (iv) green emission by triplet-to-singlet state radiative recombination of the V_O center. The model in Fig. 5(a) is consistent

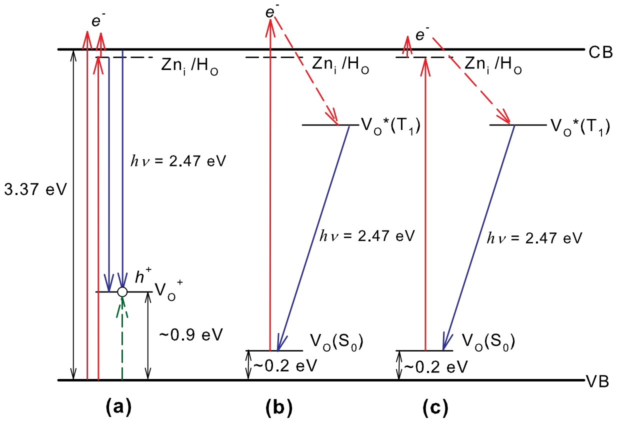

FIG. 5. Schematic depiction of possible mechanisms of GL associated with V_O center: transition from CB or shallow donor levels to a hole in V_O (a); triplet-to-singlet V_O state model for excitation above (b) and below (c) the band gap.

with GL observed in experiment when V_O is a deep donor located ∼0.9 eV above VB while the triplet-to-singlet state emission model requires V_O level to be located closer to VB, see Figs. 5(b) and 5(c). Electronic structure calculations consistently report a negative-U behavior for V_O, but there is a large scatter in their predictions of the 2+/0 transition energy. The reported values[24] fall into a broad range from 0.3 to 2.7 eV. Hence, at the present knowledge, it is hard to make any definite conclusion about the position of the V_O level. The scatter of the calculated values is, to a large extent, caused by various ways of band gap corrections. Patterson[25] employed all-electron B3LYP hybrid functional calculations which gave band gap of 3.34 eV, i.e., close to the experimental value. Interestingly, his calculations yielded the 2+/0 transition energy at ∼0.3 eV above VB, which is not far from the level required by the triplet-to-singlet state model in Figs. 5(b) and 5(c). Kodama and Uchino attributed the shallow donors to Zn_i. Although Zn_i have higher formation energy than V_O,[3] it is likely that some Zn_i were created during annealing in Zn vapor. The shallow donors could be also H_O defects, i.e., V_O associated with hydrogen. Weber and Lynn[21] showed that red coloration of ZnO occurs only when hydrogen was present during high temperature annealing in Zn vapor. Chemical analysis revealed that the as-grown ZnO crystals always contained considerable amount of hydrogen either occupying interstitial sites or forming $V_{Zn} + H$ complexes.[10] The interstitial hydrogen diffuses out of the sample at temperatures around 400 °C.[21] During annealing in Zn vapor, V_{Zn} are filled by diffusing Zn atoms. Released H atoms can be trapped at V_O introduced during Zn-annealing. Thus, it is plausible that certain fraction of V_O turned into H_O defects which are shallow donors in ZnO.[26] Hence, the shallow donor levels in Fig. 5(c) can be either Zn_i or H_O.

A tail below the PLE peak for the Zn-annealed sample in Fig. 4 extending down to 2.5 eV indicates a continuous density of states between VB and V_O level formed by Zn-annealing in the presence of hydrogen and mediating GL. This is in accordance with the red shift of the absorption edge of the transmittance curve in Fig. 3.

In summary, combination of PL and PAS studies enabled us to disclose the origin of GL in hydrothermally grown ZnO crystals. The green emission band at 2.3(1) eV is caused by $V_{Zn} + H$ complexes while the green emission at 2.47(2) eV is related to V_O centers. As-grown ZnO crystals contain $V_{Zn} + H$ complexes, and the green emission band at 2.3(1) eV is dominating. By annealing in Zn vapor, $V_{Zn} + H$ are removed from the crystal but V_O and shallow donors (Zn_i or H_O) are introduced. This makes dominating the green emission band at 2.47(2) eV.

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[1] Ü. Özgür, Y. Alivov, C. Liu, A. Teke, M. Reshchikov, S. Doğan, V. Avrutin, S. Cho, and H. Morkoç, J. Appl. Phys. **98**, 041301 (2005).

[2] F. Leiter, H. Alves, A. Hofstaetter, D. Hofmann, and B. Meyer, Phys. Status Solidi B **226**, R4 (2001).

[3] A. Kohan, G. Ceder, D. Morgan, and C. V. de Walle, Phys. Rev. B **61**, 15019 (2000).

[4] B. Guo, Z. Qiu, and K. Wong, Appl. Phys. Lett. **82**, 2290 (2003).

[5] S. Jeong, B. Kim, and B. Lee, Appl. Phys. Lett. **82**, 2625 (2003).

[6] D. Reynolds, D. Look, B. Jogai, and H. Morkoç, Solid State Commun. **101**, 643 (1997).

[7] C. Ton-That, L. Weston, and M. Phillips, Phys. Rev. B **86**, 115205 (2012).

[8] R. Krause-Rehberg and H. Leipner, *Positron Annihilation in Semiconductors* (Springer-Verlag, Berlin, 1999).

[9] Z. Q. Chen, S. Yamamoto, M. Maekawa, A. Kawasuso, X. L. Yuan, and T. Sekiguchi, J. Appl. Phys. **94**, 4807 (2003).

[10] G. Brauer, W. Anwand, D. Grambole, J. Grenzer, W. Skorupa, J. Čížek, J. Kuriplach, I. Procházka, C. C. Ling, C. K. So, D. Schulz, and D. Klimm, Phys. Rev. B **79**, 115212 (2009).

[11] E. Ohshima, H. Ogino, I. Niikura, K. Maeda, M. Sato, M. Ito, and T. Fukuda, J. Cryst. Growth **260**, 166 (2004).

[12] F. Bečvář, J. Čížek, I. Procházka, and J. Janotová, Nucl. Instrum. Methods, Phys. Res. A **539**, 372 (2005).

[13] I. Procházka, I. Novotný, and F. Bečvář, Mater. Sci. Forum **255–257**, 772 (1997).

[14] T. M. Børseth, B. Svensson, A. Kuznetsov, P. Klason, Q. Zhao, and M. Willander, Appl. Phys. Lett. **89**, 262112 (2006).

[15] F. Lukáč, J. Čížek, I. Procházka, O. Melikhova, W. Anwand, and G. Brauer, Acta Phys. Pol., A **125**, 748 (2014).

[16] F. Tuomisto, V. Ranki, K. Saarinen, and D. Look, Phys. Rev. Lett. **91**, 205502 (2003).

[17] W. Anwand, G. Brauer, R. Grynszpan, T. Cowan, D. Schulz, D. Klimm, J. Čížek, J. Kuriplach, I. Procházka, C. Ling, A. Djurišić, V. Klemm, and G. S. D. Rafaja, J. Appl. Phys. **109**, 063516 (2011).

[18] F. A. Selim, M. H. Weber, D. Solodovnikov, and K. G. Lynn, Phys. Rev. Lett. **99**, 085502 (2007).

[19] L. E. Halliburton, N. C. Giles, N. Y. Garces, M. Luo, C. Xu, L. Bai, and L. A. Boatner, Appl. Phys. Lett. **87**, 172108 (2005).

[20] M. Weber, N. Parmar, K. Jones, and K. Lynn, J. Electron. Mater. **39**, 573 (2010).

[21] M. Weber and K. Lynn, J. Phys.: Conf. Ser. **262**, 012063 (2011).

[22] M. H. Weber, F. A. Selim, D. Solodovnikov, and K. G. Lynn, Appl. Surf. Sci. **255**, 68 (2008).

[23] K. Kodama and T. Uchino, J. Appl. Phys. **111**, 093525 (2012).

[24] T. R. Paudel and W. R. L. Lambrecht, Phys. Rev. B **77**, 205202 (2008).

[25] C. H. Patterson, Phys. Rev. B **74**, 144432 (2006).

[26] E. V. Lavrov, F. Herklotz, and J. Weber, Phys. Rev. B **79**, 165210 (2009).