

Anomalous photoelectric emission from Ag on zinc-phthalocyanine film

Senku Tanaka, Tomohiro Otani, Ken Fukuzawa, Koji Ogawa, Junpei Azuma, Isamu Yamamoto, Kazutoshi Takahashi, Masao Kamada, and Ichiro Hiromitsu

Citation: [Applied Physics Letters](#) **104**, 193304 (2014); doi: 10.1063/1.4876956

View online: <http://dx.doi.org/10.1063/1.4876956>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/104/19?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Ag +12 ion induced modifications of structural and optical properties of ZnO-PMMA nanocomposite films](#)
AIP Conf. Proc. **1512**, 394 (2013); 10.1063/1.4791077

[Structural modifications of zinc phthalocyanine thin films for organic photovoltaic applications](#)
J. Appl. Phys. **111**, 103117 (2012); 10.1063/1.4721409

[Investigation on the orderly growth of thick zinc phthalocyanine films on Ag\(100\) surface](#)
J. Chem. Phys. **133**, 144704 (2010); 10.1063/1.3489658

[Anomalous enhanced Raman scattering from longitudinal optical phonons on Ag-nanoparticle-covered GaN and ZnO](#)
Appl. Phys. Lett. **96**, 033109 (2010); 10.1063/1.3291041

[Effects of coatings on temporal cathodoluminescence quenching in ZnS:Ag,Cl phosphors](#)
J. Appl. Phys. **95**, 7873 (2004); 10.1063/1.1748861

The advertisement features a photograph of the Model PS-100 probe station, a complex piece of scientific equipment with various lenses, stages, and sensors. The background is a gradient of blue. Text on the left includes 'NEW' in orange, 'Model PS-100' in large blue font, and 'Preconfigured Tabletop Probe Station' in smaller blue font. On the right, the 'Lake Shore CRYOTRONICS' logo is shown, with 'Lake Shore' in white and 'CRYOTRONICS' in blue. Below the logo, the tagline 'An affordable solution for a wide range of research' is written in white italicized font.

Anomalous photoelectric emission from Ag on zinc-phthalocyanine film

Senku Tanaka,^{1,a)} Tomohiro Otani,² Ken Fukuzawa,² Koji Ogawa,³ Junpei Azuma,³ Isamu Yamamoto,³ Kazutoshi Takahashi,³ Masao Kamada,³ and Ichiro Hiromitsu²

¹*Department of Electric and Electronic Engineering, Faculty of Science and Engineering, Kinki University, Higashiosaka 577-8502, Japan*

²*Department of Physics and Materials Science, Graduate School of Science and Engineering, Shimane University, Matsue 690-8504, Japan*

³*Synchrotron Light Application Center, Saga University, Saga 840-8502, Japan*

(Received 6 March 2014; accepted 4 May 2014; published online 13 May 2014)

Photoelectric emission from organic and metal thin films is generally observed with irradiation of photon energy larger than 4 eV. In this paper, however, we report photoelectric emission from Ag on a zinc-phthalocyanine (ZnPc) layer at a photon energy of 3.4 eV. The threshold energy for this photoelectric emission is much smaller than the work function of Ag estimated by conventional photoelectron spectroscopy. The photoelectric emission by low-energy photons is significant for Ag thicknesses of less than 1 nm. Photoelectron spectroscopy and morphological study of the Ag/ZnPc suggest that the anomalous photoelectric emission from the Ag surface is caused by a vacuum level shift at the Ag/ZnPc interface and by surface plasmons of the Ag nanoparticles.

© 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4876956>]

An important issue in developing organic electronic devices is the control of the properties of organic/organic and metal/organic interfaces. It is known that the properties of these interfaces affect the performance of the final organic electronic device. For example, vacuum level shift is often observed at organic/organic and metal/organic interfaces,^{1–5} and many studies have indicated that this shift affects the efficiency of carrier injection or extraction at such interfaces.^{6–8} While past studies have focused on the effect of the vacuum level shift on the electronic properties of organic electronic devices, the effect on the barrier height for photoelectric emission has been paid little attention. In this paper, we report photoelectric emission from a metal surface on an organic layer under irradiation with near-UV light having an energy of less than 4 eV. In general, the work function of thin films of metals, except alkali metals, and the ionization potential of organic thin films are no less than 4 eV. It is therefore expected that light energy of less than 4 eV cannot generate photoelectric emission from the surfaces of metal or organic films. From the results of photoelectron spectroscopy, we conclude that the vacuum level shift at the metal/organic interface is correlated with a decrease in the effective threshold energy for photoelectric emission from the sample surface. The effect of metal surface plasmons on the anomalous photoelectric emission is also discussed.

Zinc-phthalocyanine (ZnPc) was used as the organic layer in this work. ZnPc is a typical small-molecule semiconductor used in organic solar cells. The ZnPc was purchased from Kanto Chemical and sublimed three times for purification. ZnPc thin films were fabricated by vacuum deposition on an indium tin oxide (ITO) substrate purchased from GEOMATEC. The pressure used during the deposition was in the range of 10^{-5} Pa. Ag was used as the metal layer on the ZnPc film. The thicknesses of the ZnPc and Ag layers were measured using a quartz microbalance. The values of

the thickness noted in this paper are, therefore, nominal ones. The photoelectric emission by low-energy photo-irradiation and the photoelectron spectra under high-energy excitation of the film were measured using an experimental photoelectron spectroscopy setup. The photoelectron spectroscopy was performed at two synchrotron facilities (Beam line 8B, UVSOR, Institute for Molecular Science, Okazaki, Japan, and Beam line 13, SAGA-LS, Kyushu Synchrotron Light Research Center, Tosu, Japan). Both beam lines are equipped with a photoelectron measurement chamber connected to a preparation chamber. Thus, the samples could be transferred from the preparation chamber to the measurement chamber without breaking the vacuum. A white light source (a Xe lamp with an air mass 1.5 filter, HAL-320, Asahi Spectra Co. Ltd.) and a tunable Ti:sapphire laser (Chameleon, COHERENT, Inc.) were used as UV-visible region light sources. The UV-visible light was introduced to the measurement chamber through a glass viewport that cut off the light with wavelength shorter than approximately 320 nm. The power of the white light on the sample surface was 100 ± 10 mW/cm². The repetition rate of the second harmonic generation of the Ti:sapphire laser was 80 MHz, and the spot size and the intensity of the laser pulse were 7 mm in diameter and 0.2–0.5 nJ, respectively.

Figure 1(a) shows the photoelectron spectra of the Ag (0.2 nm)/ZnPc (10 nm)/ITO sample under laser irradiation of different wavelengths. The abscissa indicates the kinetic energy of the electron. Note that a bias voltage of -10.0 V was applied to the sample to detect the electrons near the vacuum level. The wavelength dependence of the intensity of the photoelectric emission is shown in Fig. 1(b). The threshold wavelength for the emission was estimated to be around 370 nm. By taking the spectral width of the irradiated laser (approximately 10 nm) into account, the threshold energy of the photoelectric emission of the sample surface was estimated to be approximately 3.4 eV. This value is substantially smaller than both the ionization potential of the ZnPc thin film and the work function of the Ag film, which were estimated to

^{a)} Author to whom correspondence should be addressed. Electronic mail: senku@ele.kindai.ac.jp

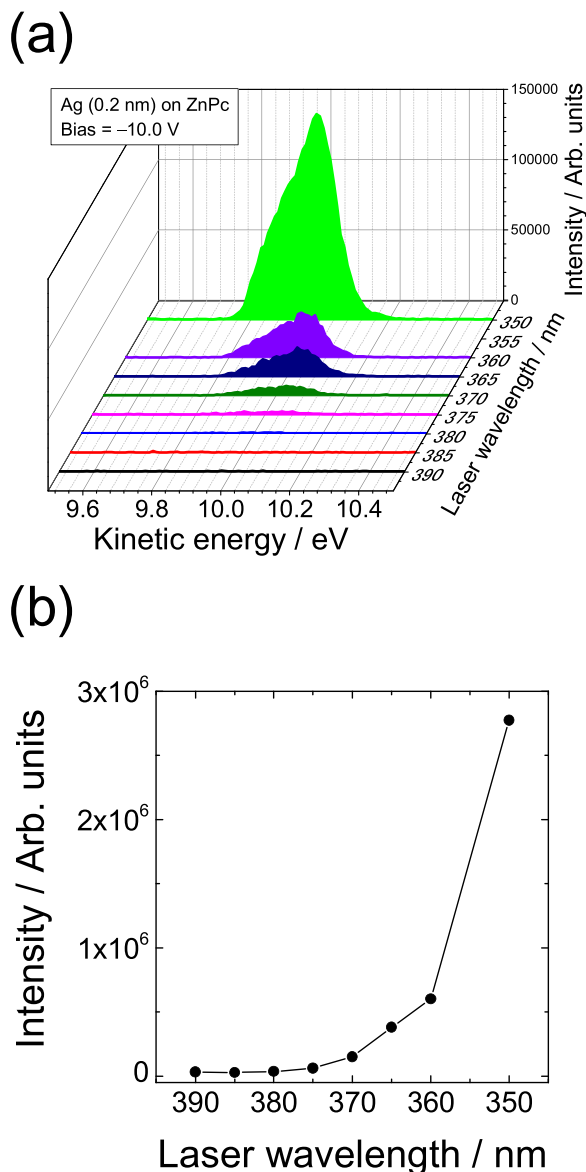


FIG. 1. (a) Photoelectron spectra of the Ag(0.2 nm)/ZnPc sample under laser irradiation of different individual wavelengths. The sample was biased at -10.0 V. (b) Intensities of the photoelectron peak under irradiation of the individual laser wavelengths.

be 5.1 eV and 4.1 eV, respectively, from the conventional photoelectron measurements discussed later.

To investigate the mechanism of this anomalous photoelectric emission from Ag/ZnPc, the electronic structure of the Ag/ZnPc interface was observed by photoelectron spectroscopy using synchrotron radiation. Fig. 2 shows the variation in the photoelectron spectrum of the ZnPc thin film (15 nm) during the incremental deposition of Ag. All photoelectron measurements were carried out at room temperature with synchrotron radiation of 39.6 eV. The overall energy resolution was approximately 0.15 eV. The bottom spectrum is the photoelectron spectrum of the ZnPc film (15 nm) on the ITO substrate. The Ag thickness increases from the bottom to the top. The left panel shows the photoelectron spectra of the secondary electron cutoff, for which a bias voltage of -5.0 V was applied to detect the photoelectrons near the vacuum level. The secondary electron cutoff was shifted approximately 0.25 eV toward lower kinetic energy by

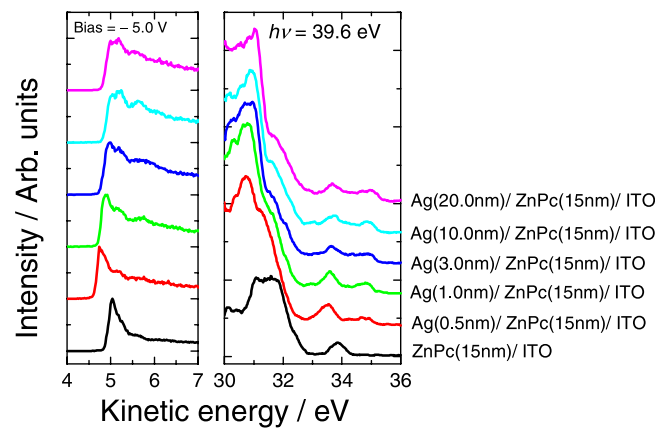


FIG. 2. Variation of the photoelectron spectra of the ZnPc film under incremental Ag deposition (0.5, 1.0, 3.0, 10.0, 20.0 nm). Left panel: Secondary electron cutoff region. The sample was biased at -5.0 V during the measurements. Right panel: Around the Fermi level. No bias voltage was applied to the sample.

deposition of 0.5 nm Ag, and then shifted toward higher kinetic energy with increasing Ag thickness. The right panel shows the photoelectron spectra near the Fermi level. (Note that no bias voltage was applied to the sample for the photoelectron measurement near the Fermi level.) The peak at around 34 eV is attributed to the highest occupied molecular orbital (HOMO) of ZnPc. The step at 35.3 eV in the photoelectron spectrum measured after Ag deposition is due to the Fermi level. The HOMO peak of ZnPc showed a similar variation with increasing Ag thickness to that of the secondary electron cutoff. The smallest work function of 3.9 eV was observed for Ag (0.5 nm)/ZnPc (15 nm). The shift of the secondary electron cutoff by the deposition of Ag was observed also on the sample in Fig. 1 by the conventional photoelectron spectroscopy using synchrotron radiation. The secondary electron cutoff was shifted approximately 0.35 eV toward lower kinetic energy by deposition of 0.2 nm Ag on the ZnPc substrate.⁹

From the photoelectron spectroscopy results, the shift in the secondary electron cutoff was considered to be a key factor in the anomalous photoelectric emission. The variation of the secondary electron cutoff was basically correlated with the shift in the vacuum level of the sample surface. Thus, to investigate the correlation between the variation of the vacuum level and the anomalous photoelectric emission, the dependence of the photoelectric emission intensity on Ag thickness was observed under white light illumination. The results are shown in Fig. 3. The maximum emission intensity was observed for an Ag thickness of 0.5 nm. The intensity of the photoelectric emission decreased with further increases in Ag thickness. The Ag thickness dependence of the vacuum level shift estimated from Fig. 2 is plotted in Fig. 3. The value of the vacuum level shift was evaluated against the vacuum level of the ZnPc film. The emission intensity was negatively correlated with the vacuum level shift. The present results infer that a decrease in the vacuum level, which indicates a decrease in the effective work function, of the Ag on the ZnPc surface is the key factor accounting for the anomalous photoelectric emission.

Vacuum level shift at metal/organic interfaces has been reported in many systems, and is attributed to the formation

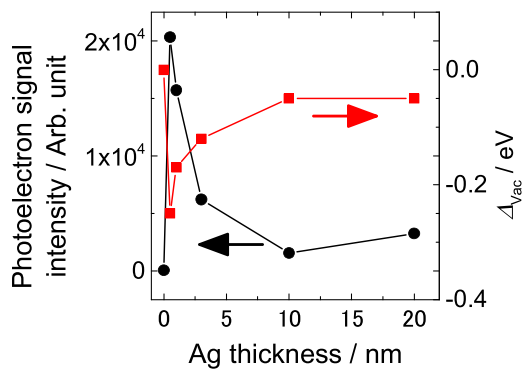


FIG. 3. Ag thickness dependence of the photoelectron signal intensity (black circles) and the vacuum level shift (ΔV_{vac}) (red squares).

of an interfacial dipole layer.^{1–5} Several mechanisms have been proposed as to the origin of this interfacial dipole.^{2,10,11} In the present case, weak chemical interaction between ZnPc and Ag is probably the main mechanism. The shape of the HOMO peak of ZnPc showed no significant change after the deposition of Ag. A strong chemical interaction may distort the shape of the HOMO peak.¹² From the direction of the vacuum level shift at the Ag/ZnPc interface, it is expected that an interfacial dipole layer was formed with the positively charged Ag and the negatively charged ZnPc. Note that the interfacial dipole was localized at the Ag/ZnPc interface. The effect of this interfacial dipole on the vacuum level shift at the surface decreased with increasing Ag thickness. The effective barrier height for the photoelectric emission was therefore smallest for the smallest Ag thickness and increased with Ag thickness. In addition, the dispersion of Ag in the ZnPc layer may have disturbed the effect of the interfacial dipole. In Fig. 2, the HOMO peak of ZnPc appears in the spectrum of the Ag (20 nm)/ZnPc sample. Photoelectron spectroscopy is a surface-sensitive technique because of the short mean-free path of the photoelectron in the solid; an electron with a kinetic energy of 30–40 eV has a mean-free path of only a few nanometers. Thus, the presence of the HOMO peak of ZnPc in the Ag (20 nm)/ZnPc spectrum suggested that part of the ZnPc remained near the sample surface even after the deposition of thick Ag. We suppose Ag particles during the vacuum deposition have a large momentum and may diffuse into the ZnPc layer. Indeed, the migration of metal particles into organic layers during thermal deposition has been reported.¹³ A disordered distribution of the Ag particles in the ZnPc layer can disturb the formation of the aligned interfacial dipole.

Next, we discuss potential mechanisms of the anomalous photoelectric emission other than the interfacial dipole. As described, the work function of the Ag (0.5 nm)/ZnPc (15 nm) film was estimated to be 3.9 eV by the photoelectron spectroscopy. There is obvious deviation from the threshold energy for the anomalous photoelectric emission (3.4 eV). Other probable mechanisms accounting for photoelectric emission at smaller photon energy than the work function of the individual materials include two-photon photoelectron emission (2PPE),^{14–16} exciton fusion,¹⁷ and surface-plasmon-assisted (SPA) photoemission.^{18,19}

In general, the 2PPE process is observed under high concentrations of light created by high-intensity laser light with

femtosecond-order pulse width. In the present measurement, the photon concentration was too small to cause 2PPE. In addition, in the case of 2PPE, the photoelectron intensity should be proportional to the square of the light intensity. The light power dependence of the photoelectric emission intensity of the Ag (0.5 nm)/ZnPc (15 nm) sample is shown in Fig. 4. The emission intensity was linearly dependent on the light intensity. This result indicates that the observed photoelectric emission was the result of a single-photon process. Moreover, the photoelectron spectrum caused by 2PPE would have a relatively long tail toward higher kinetic energy. The spectral width of the present anomalous photoelectric emission was less than 0.3 eV with no tail at higher kinetic energy, as seen in Fig. 1. These results exclude the possibility of 2PPE in the present phenomenon. For exciton fusion, the photoelectron intensity should also be increased by the square of the light power.¹⁷ Exciton fusion is therefore also excluded as the origin of the present anomalous photoemission.

SPA photoemission is an enhancement of photoemission yield in the range of surface-plasmon absorption of metal surfaces. Callcott and Arakawa have demonstrated the enhancement of the photoemission yield of thin films of Al by surface-plasmon resonance.¹⁸ Koschmieder and Thompson have also reported that the incident energy dependence of the photoemission yield from (4-methyl pyridine)-covered Ag films showed peaks at the surface and the bulk plasmon resonance.¹⁹ Although anomalous photoelectric emission was not observed in either case, these studies suggest that surface plasmons affect the photoelectric emission in the range of the plasmon resonance. In general, Ag surface plasmons are excited by light of around 400 nm in wavelength. In the consideration of surface plasmons, the structure of Ag on the sample surface is important. To investigate the structure of the Ag/ZnPc surface, we observed the morphology of the Ag on the ZnPc surface using atomic force microscopy (AFM) and transmission electron microscopy (TEM). For AFM measurements, the sample consisting of Ag (0.5 nm)/ZnPc (20 nm) on ITO substrate was examined. Ag particles of less than 10 nm in diameter were found to be dispersed on the ZnPc grains.⁹

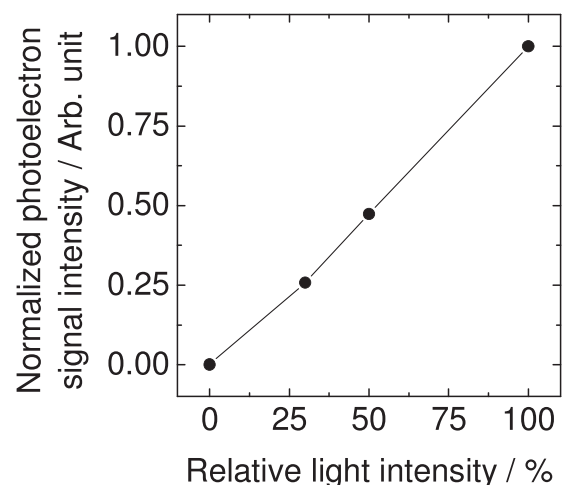


FIG. 4. Light intensity dependence of the intensity of the photoelectron signal from the Ag (0.5 nm)/ZnPc (15 nm) sample under white light irradiation. The intensity of the photoelectron signal has been normalized to that of the 100% value.

As mentioned above, the Ag thickness measured by the quartz microbalance was nominal. Thus, it was possible that the Ag existed on the ZnPc layer in the form of small particles having sizes in the range of the small thickness. The TEM image of the sample consisting of Ag (0.5 nm)/ZnPc (10 nm) on carbon grid also showed a similar structure.⁹ The average cross-sectional size of the Ag particles on the ZnPc surface was approximately 5 nm. It has been reported that free Ag clusters of 6–30 nm in size show surface-plasmon absorption at around 3.4–3.7 eV.²⁰ The surface plasmons of Ag on ZnPc may also be generated by absorption of light of similar energy range, although the resonance energy for these surface plasmons would differ from that of free Ag clusters. Tatsuma and co-workers have proposed the occurrence of plasmon-induced charge separation between TiO₂ and Ag nanostructures.^{21,22} A similar mechanism may have assisted the escape of the electrons from the Ag to the vacuum. At this point, the effect of the SPA photoemission on the anomalous photoelectric emission is not clear. However, the discrepancy between the work function of the sample estimated by photoelectron spectroscopy and the threshold energy of the anomalous photoelectric emission infers that the energy of the probe light may affect the process of electron escape from solid surfaces. Further research is now in progress.

In conclusion, we have demonstrated that anomalous photoelectric emission from an Ag/ZnPc surface occurs under 3.4 eV light irradiation. Although the reason for the discrepancy observed between the threshold energy of the photoelectric emission (3.4 eV) and the estimated work function of the surface by synchrotron photoelectron spectroscopy (3.9 eV) is not yet clear, a decrease in the effective work function of Ag caused by the interfacial dipole at the Ag/ZnPc interface and SPA photoemission are probably the key mechanisms of the anomalous photoelectric emission. From an application viewpoint, the present phenomenon may be useful for the fabrication of photodiodes or photocathodes that work in the near-UV region. The simple structure and preparation method of this system are additional advantages for such applications. For example, the present work may be applicable to the fabrication of a planar electron source. It would also be interesting to combine this

system with a transparent flexible substrate, such as an ITO-coated polyethylene terephthalate film.

The authors thank Dr. Kazuto Arakawa at Shimane University for TEM imaging and fruitful discussions. Part of this work was supported by JSPS KAKENHI Grant No. 24656037, Research Grant of Murata Science Foundation, Kyushu Nanotechnology Network support, and the Use-of-UVSOR Facility Program (BL8B, 2011–2012) of the Institute for Molecular Science, Okazaki, Japan.

- ¹H. Ishii and K. Seki, *IEEE Trans. Electron Devices* **44**, 1295–1301 (1997).
- ²H. Ishii, K. Sugiyama, E. Ito, and K. Seki, *Adv. Mater.* **11**, 605–625 (1999).
- ³I. G. Hill, D. Milliron, J. Schwartz, and A. Kahn, *Appl. Surf. Sci.* **166**, 354–362 (2000).
- ⁴L. Yan and Y. Gao, *Thin Solid Films* **417**, 101–106 (2002).
- ⁵N. Koch, *ChemPhysChem* **8**, 1438–1455 (2007).
- ⁶T. Mori, H. Fujikawa, S. Tokito, and Y. Taga, *Appl. Phys. Lett.* **73**, 2763–2765 (1998).
- ⁷S. T. Lee, Y. M. Wang, X. Y. Hou, and C. W. Tang, *Appl. Phys. Lett.* **74**, 670–672 (1999).
- ⁸S. Tanaka, T. Hanada, K. Ono, K. Watanabe, K. Yoshino, and I. Hiromitsu, *Appl. Phys. Lett.* **97**, 253306 (2010).
- ⁹See supplemental material at <http://dx.doi.org/10.1063/1.4876956> for the photoelectron spectra and the morphology of Ag on the ZnPc surface.
- ¹⁰H. Vazquez, F. Flores, and A. Kahn, *Org. Electron.* **8**, 241–248 (2007).
- ¹¹M. T. Greiner, M. G. Helander, W.-M. Tang, Z.-B. Wang, J. Qiu, and Z.-H. Lu, *Nature Mater.* **11**, 76–81 (2012).
- ¹²T. Schwieger, H. Peisert, M. S. Golden, M. Knupfer, and J. Fink, *Phys. Rev. B* **66**, 155207 (2002).
- ¹³K. Suemori, M. Yokoyama, and M. Hiramoto, *J. Appl. Phys.* **99**, 036109 (2006).
- ¹⁴C. D. Lindstrom and X.-Y. Zhu, *Chem. Rev.* **106**, 4281–4300 (2006).
- ¹⁵M. Cinchetti, D. A. Valdaitsev, A. Gloskovskii, A. Oelsner, S. A. Nepijko, and G. Schönhense, *J. Electron Spectrosc. Relat. Phenom.* **137–140**, 249–257 (2004).
- ¹⁶A. Gloskovskii, D. A. Valdaitsev, M. Cinchetti, S. A. Nepijko, J. Lange, M. Aeschlimann, M. Bauer, M. Klimentov, L. V. Viduta, P. M. Tomchuk, and G. Schönhense, *Phys. Rev. B* **77**, 195427 (2008).
- ¹⁷M. Ono, R. Katoh, and M. Kotani, *Proc. SPIE* **2362**, 219–224 (1995).
- ¹⁸A. Callcott and E. T. Arakawa, *Phys. Rev. B* **11**, 2750–2758 (1975).
- ¹⁹T. H. Koschmieder and J. C. Thompson, *Phys. Rev. B* **50**, 7845–7850 (1994).
- ²⁰K.-P. Charlé, L. König, S. Nepijko, I. Rabin, and W. Schulze, *Cryst. Res. Technol.* **33**, 1085–1096 (1998).
- ²¹Y. Tiana and T. Tatsuma, *Chem. Commun.* **2004**, 1810–1811.
- ²²E. Kazuma, N. Sakai, and T. Tatsuma, *Chem. Commun.* **47**, 5777–5779 (2011).