A combined first principle calculations and experimental study on the spin-polarized band structure of Co-doped PbPdO2

S. W. Chen, S. C. Huang, G. Y. Guo, S. Chiang, J. M. Lee, S. A. Chen, S. C. Haw, K. T. Lu, and J. M. Chen

A combined first principle calculations and experimental study on the spin-polarized band structure of Co-doped PbPdO$_2$

S. W. Chen,[1] S. C. Huang,[2] G. Y. Guo,[3,4,a)] S. Chiang,[5] J. M. Lee,[1] S. A. Chen,[1] S. C. Haw,[1] K. T. Lu,[1] and J. M. Chen[1,a)]

[1]National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan
[2]Department of Physics, National Tsing Hua University, Hsinchu 30013, Taiwan
[3]Graduate Institute of Applied Physics, National Chengchi University, Taipei 11605, Taiwan
[4]Department of Physics, National Taiwan University, Taipei 10617, Taiwan
[5]Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180, USA

With x-ray spectroscopy and first-principles calculations, we expose the electronic structure, near the Fermi level, of Co-doped PbPdO$_2$ composed of O 2p-Pd 4d hybridized states with an additional contribution of a spin-polarized Co 3d state at either a greater or smaller energy. The spin-polarized Co 3d states interacting with O 2p-Pd 4d hybridized states cause spin splitting at the band edge. Fascinating physical properties such as high-temperature ferromagnetism thus arise in Co-doped PbPdO$_2$. Results will help in the design of materials with desired electronic structures and the control of spin polarization with chemical doping. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4768293]

The manipulation of spin degrees of freedom has been a primary issue for the development of spin electronic devices. Half-metals are important for the generation of spin-polarized carriers because of their highly spin-asymmetric electronic structure,[1] but in practice, a small spin-relaxation length limits their applications. Magnetic semiconductors with a large spin-relaxation length are also candidates for spintronics,[2] but the spin polarization in those materials is too small to be utilized.

Wang et al. recently reported an oxide gapless semiconductor PbPdO$_2$.[3,4] The gapless characteristic makes it sensitive to the external or internal environments, such as temperature, magnetic field, and doping carrier. PbPdO$_2$ can thus serve as a suitable matrix for the development of material systems with desired electronic structures and physical properties.[5] In particular, Co-doped PbPdO$_2$ exhibits such extraordinary properties as colossal electroresistance (CER),[4] giant magnetoresistance (GMR),[4,6,7] and unusually high-temperature ferromagnetic effects.[8] Co-doped PbPdO$_2$ exhibits also both spin polarization and a large spin-relaxation length, making it attractive as a prospective spintronic material after the development of half-metals and diluted magnetic semiconductors.

The intriguing physical properties of Co-doped PbPdO$_2$ are closely related to its unique band structure that exhibits spin-gapless characteristics. Several authors have proposed theoretically that the spin-gapless feature becomes generated on introducing foreign ions or vacancies into a gapless or narrow-gap material, consequently altering its corresponding electronic structure.[4,8,9] However, up to now, the electronic structure and the origin of physical properties of spin-gapless semiconductor Co-doped PbPdO$_2$ have been rarely discussed because of a lack of both experimental evidence and knowledge about the variation of electronic structure with element doping. Only

when one is equipped with a comprehensive understanding of electronic structure can one realize how to design material systems with desired characteristics; the fundamental mechanism of physical properties can thereby be deduced. In this work, we explore the electronic structure of Co-doped PbPdO$_2$ in detail with x-ray absorption spectroscopy (XAS) and photoemission spectroscopy (PES) complemented with calculations of electronic structure. With highly consistent experimental data and calculated results, the spin-splitting band structure of Co-doped PbPdO$_2$ clearly emerges. Based on these complementary results, clues appear about how to tune the band structure and spin polarization with chemical doping. An opportunity arises also to expound the mechanism of fascinating physical properties of Co-doped PbPdO$_2$, such as its unusually high-temperature ferromagnetism.[8]

To obtain Co-doped PbPdO$_2$, the precursor of PdCoO$_2$ was synthesized with a process involving cation exchange.[10] With a solid-state method, PbPd$_{(1-x)}$Co$_x$O$_2$ ($x = 0.1$, 0.15, and 0.25) was then synthesized from a stoichiometric mixture of PbO, PdO, and PdCoO$_2$ powders. XAS and PES spectra were recorded at the 20A1 beamline of the National Synchrotron Radiation Research Center in Taiwan. Theoretical calculations on a series of Co-doped PbPdO$_2$ were made with the supercell approach. As for pure PbPdO$_2$,[5] we adopted a simple orthorhombic structure with four formula units per unit cell for PbPd$_{0.75}$Co$_{0.25}$O$_2$ with one Pd atom replaced by a Co atom. For PbPd$_{0.875}$Co$_{0.125}$O$_2$, we used an orthorhombic supercell with the cell size along the z-axis twice that for pure PbPdO$_2$ and PbPd$_{0.75}$Co$_{0.25}$O$_2$. One of eight Pd atoms was then substituted with a Co atom. The structures were then optimized with an accurate frozen-core projector augmented-wave (PAW) method,[11] as implemented in the Vienna ab initio simulation package (VASP),[12,13] based on density-functional theory (DFT)[14] with the generalized gradient approximation (GGA)[15] plus an on-site Coulomb interaction U.[16] The structural optimizations were implemented

---

a)Authors to whom correspondence should be addressed. Electronic addresses: jmchen@nsrrc.org.tw and gyguo@phys.ntu.edu.tw.
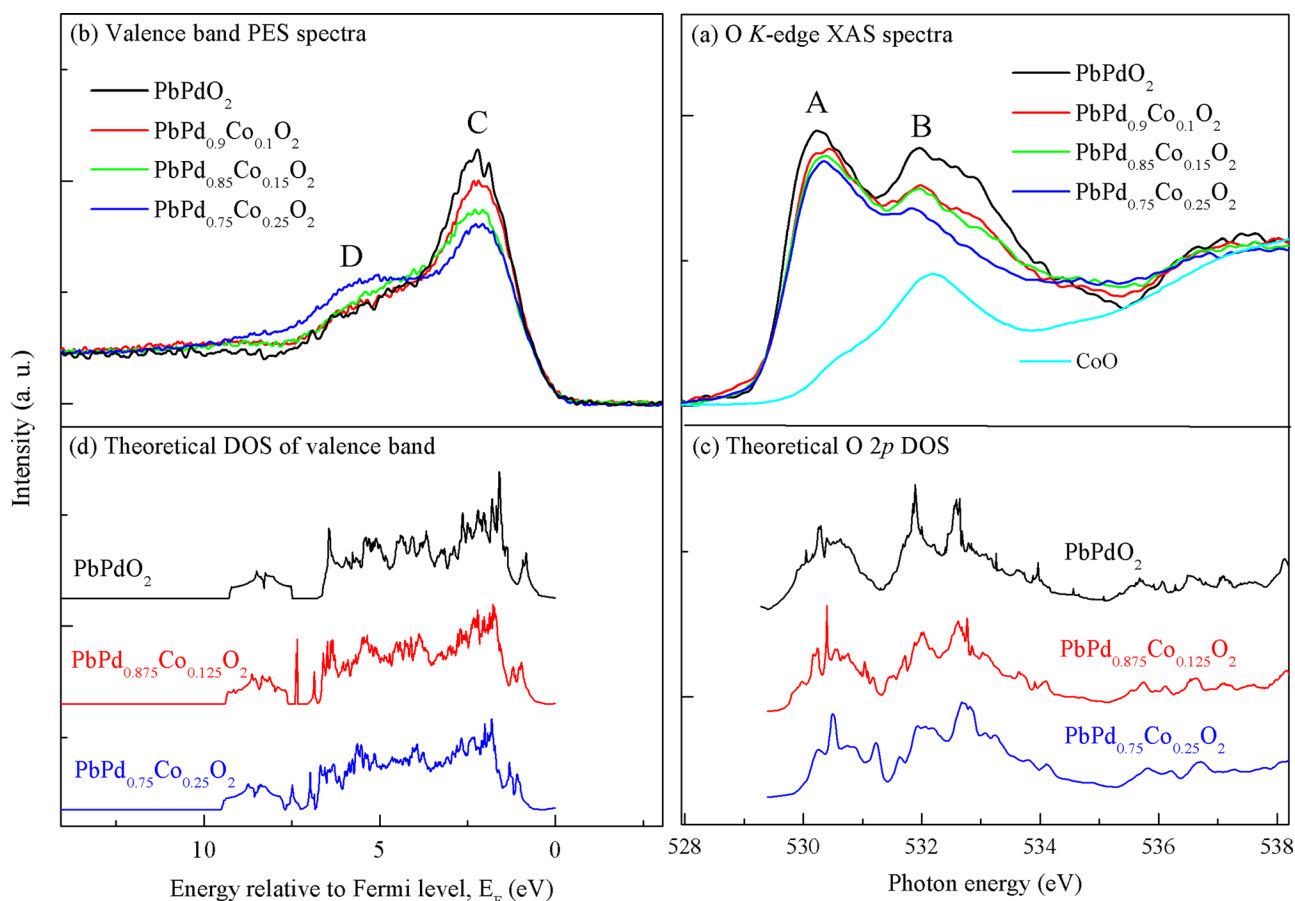
© 2012 American Institute of Physics

FIG. 1. (a) O *K*-edge absorption spectra, (b) valence band PES spectra recorded with photon energy 650 eV, (c) calculated O 2p density of states above the Fermi level, and (d) calculated total density of states below the Fermi level, of Co-doped $PbPdO_2$.

with truncation energy 550 eV for plane waves, and a $8 \times 12 \times 12$ ($8 \times 12 \times 8$) k-point grid for $PbPd_{0.75}Co_{0.25}O_2$ ($PbPd_{0.875}Co_{0.125}O_2$). After structural optimization, the final self-consistent electronic band structures were calculated with a finer $10 \times 20 \times 20$ ($10 \times 20 \times 10$) k-point grid for $PbPd_{0.75}Co_{0.25}O_2$ ($PbPd_{0.875}Co_{0.125}O_2$). The details of experimental procedures and calculation parameters were given in the supplementary material.[17]

Figure 1(a) shows the O *K*-edge XAS spectra of parent $PbPdO_2$ and Co-doped $PbPdO_2$; the spectrum of CoO is plotted for comparison. As displayed, the O *K*-edge spectrum of parent $PbPdO_2$ consists of mainly two features labeled A and B. In our preceding work, these two features were ascribed to electronic excitation from O 1*s* to O 2*p*-Pd 4*d* hybridized states based on calculations and experimental data.[5] Herein, we observed further that the intensity of these two features decreased with Co doping into $PbPdO_2$; in particular, the decrease of the intensity of feature B is much greater than that of feature A, as indicated in Fig. 1(a). Feature B, which has an energy near the main feature of the CoO standard, reflects mainly the additional contribution of O 2*p* and Co 3*d* hybridization to the weaker covalent interaction. In contrast, feature A, with a slightly decreased intensity, then reflects the result of Pd substitution by Co atoms. These results demonstrate clearly that the conduction-band structure near the Fermi level of Co-doped $PbPdO_2$ is composed mainly of O 2*p*-Pd 4*d* hybridized bands with an additional contribution of a Co 3*d* state at a greater energy.

To examine the electronic structure below the Fermi level, Fig. 1(b) shows the valence-band PES spectra of parent $PbPdO_2$ and Co-doped $PbPdO_2$. As displayed, the PES spectrum of parent $PbPdO_2$ exhibits one pronounced feature, labeled C, with a maximum about 2.5 eV below the Fermi level, assigned to the O 2*p* and Pd 4*d* hybridized band as established previously.[5] With Co doping into $PbPdO_2$, the intensity of this pronounced feature decreased, reflecting the decreased concentration of Pd through the substitution of Pd by Co atoms. We observed also an additional feature, formed when Co was doped into $PbPdO_2$, contributing to the intensity of the feature, labeled D, situated about 6 eV below the Fermi level. The intensity of this feature increased gradually with increasing Co concentration. To characterize this feature, we measured Co *L*-edge (2*p*-3*d*) resonant photoemission spectra at various energies determined by the Co 2*p* XAS profile. With a photon energy about the Co 2*p*-3*d* core threshold that excites 2*p* core electrons to the outer 3*d* states, resonant photoemission thus manifests the Co 3*d* states in the valence-band spectra with enhanced intensity.[18] (See supplementary material[17]) In that way, we confirm the formed feature, from Co doping, about 6 eV below the Fermi level to be the Co 3*d* state. Taken together, the PES and XAS define well the electronic structure near the Fermi level of Co-doped $PbPdO_2$. The electronic structure near the Fermi level of Co-doped $PbPdO_2$ is composed mainly of O 2*p*-Pd 4*d* hybridized bands with an additional contribution of Co 3*d* states at an either greater or smaller energy relative to the Fermi level.
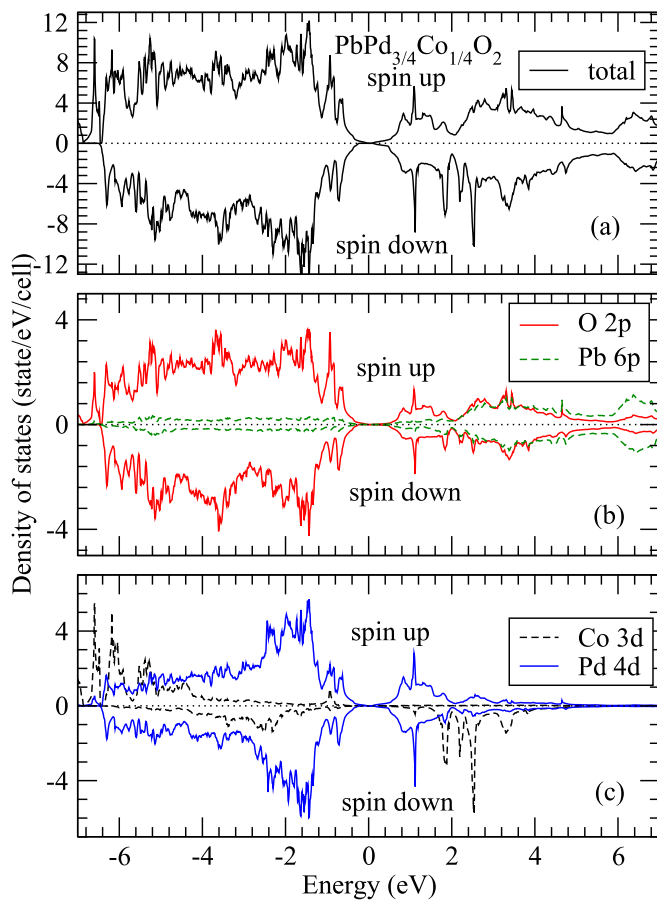
FIG. 2. Total and site-decomposed densities of states of Pb, Pd, Co, and O in $PbPd_{0.75}Co_{0.25}O_2$.

In addition to the spectral analyses, we undertook calculations of the electronic structure to verify the deduced information about the band structure. The calculated O $2p$ densities of states are satisfactorily consistent with the O K-edge XAS spectra of Co-doped $PbPdO_2$, as indicated in Fig. 1(c); the calculated total densities of states satisfactorily reproduce the overall features in the valence-band PES spectra displayed in Fig. 1(d). We calculated also the spin-resolved densities of states of Co-doped $PbPdO_2$ shown in Figure 2. The evident characteristic is the opposite spin states of Co $3d$ bands in the valence and conduction bands, respectively: Co $3d$ states in the valence band primarily exhibit spin-up character whereas Co $3d$ states in the conduction band exhibit predominantly spin-down character.

Figure 3 shows the calculated band structure of parent $PbPdO_2$ and Co-doped $PbPdO_2$. As displayed in Fig. 3(a), the parent $PbPdO_2$ shows a gapless band structure: there is no gap between the valence band and the conduction band. On doping 0.125 mole Co into $PbPdO_2$, a spin-gapless band structure is obtained. One spin channel is gapless whereas the other spin channel is semiconducting, as shown in Fig. 3(b), consistent with the spin-gapless band structure theoretically proposed by Wang.[3] As the concentration of the doped Co was increased to 0.25 mole, a band gap opened in Co-doped $PbPdO_2$ and caused spin splitting at both the top of valence band and the bottom of the conduction band. The spin-up and spin-down densities of states are separated mutually as shown in Fig. 3(c). Spin-split states are composed mainly of Pd $4d$ and O $2p$ hybridized bands. Actually, spin splitting at the band edge has been observed in several
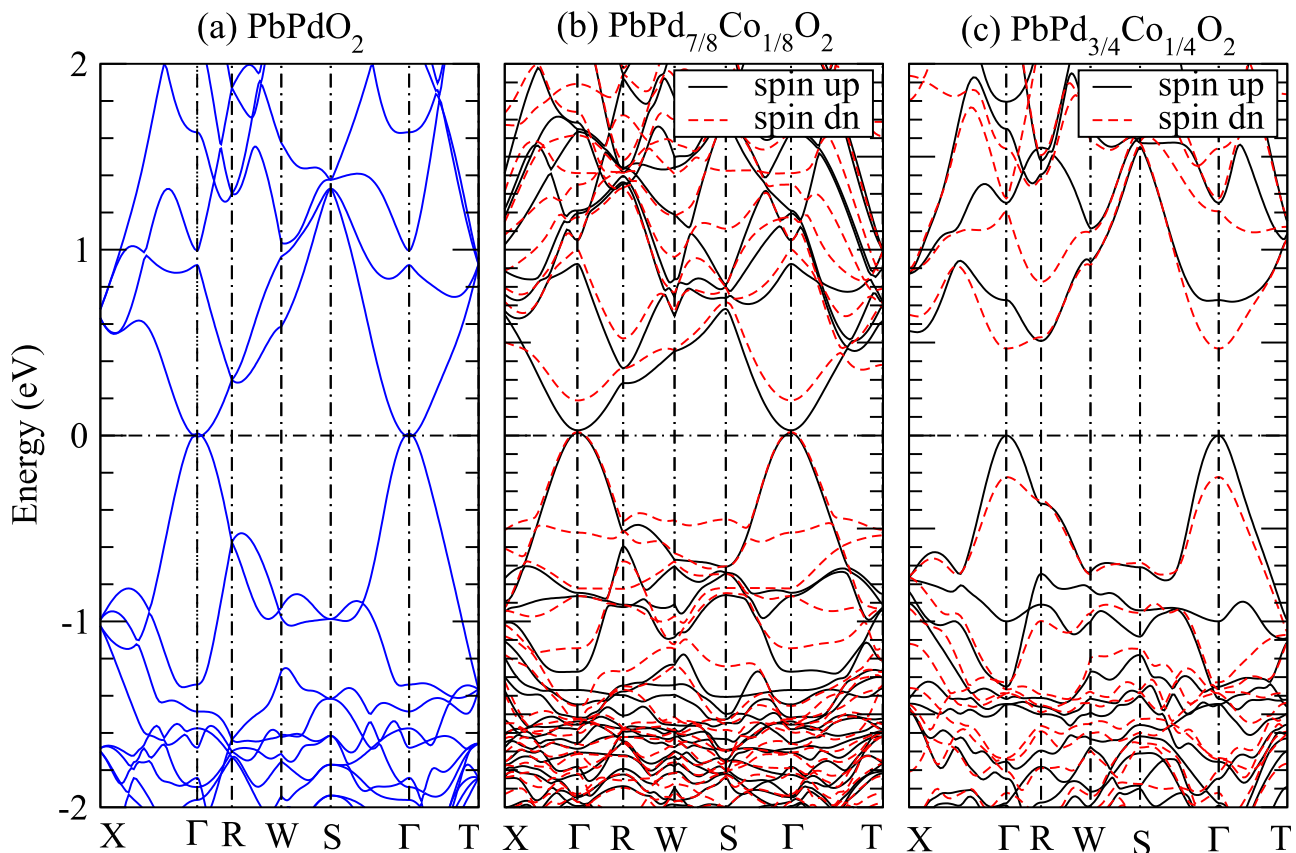

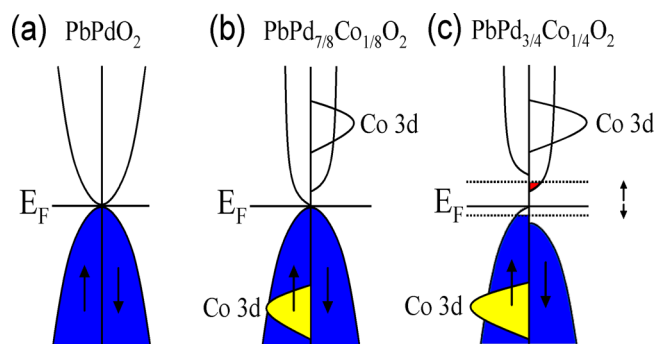FIG. 3. Band structures of (a) parent $PbPdO_2$, (b) $PbPd_{7/8}Co_{1/8}O_2$, and (c) $PbPd_{3/4}Co_{1/4}O_2$.

FIG. 4. Sketch of the spin-polarized band structure of (a) parent $PbPdO_2$, (b) $PbPd_{7/8}Co_{1/8}O_2$, and (c) $PbPd_{3/4}Co_{1/4}O_2$, with thermal excitation and tuning the Fermi level.

systems such as electron-doped EuO or EuS and magnetic semiconductor Mn-doped GaAs.[19,20] The origin of spin splitting was attributed to the doped magnetic ions polarizing the conduction and/or valence band by exchange interaction.[19–23] Analogously, in Co-doped $PbPdO_2$, the spin-polarized Co $3d$ states would interact with the Pd $4d$-O $2p$ hybridized states, causing the spin splitting at the top of the valence band and the bottom of the conduction band. This exchange interaction is based on the covalent hybridization between Co $3d$-O $2p$ bands and Pd $4d$-O $2p$ bands, as is evident in the O K-edge XAS spectra in Fig. 1.

Figure 4 displays schematically the band structures of parent $PbPdO_2$ and Co-doped $PbPdO_2$. With the formation of the spin-split band structure, Co-doped $PbPdO_2$ can thus exhibit several fascinating physical properties,[4,6–8] such as unusually high-temperature ferromagnetism. Ferromagnetism would be related closely to the spin-split states at the band edge similar to the systems of half-metals[21,24] and magnetic semiconductors.[20,22,23,25] In such systems, polarized carriers and ferromagnetic ordering were obtained as the Fermi level crossed the spin-split states. Spin-split states thus generate possible applications in spintronic devices. In Co-doped $PbPdO_2$, thermal excitation increases the carriers, in the spin-split state of the conduction band, equipped with full spin polarization as presented in Fig. 4(c). Accordingly, the spin-split state near the band edge is likely responsible for the unusually high-temperature ferromagnetism in Co-doped $PbPdO_2$. Besides, fully spin-polarized carriers are expected also to be obtained on precisely controlling the Fermi level across the spin-split states as indicated in Fig. 4(c). Emission of fully circularly polarized light might also occur in Co-doped $PbPdO_2$, when the relaxation of the excited carriers is restricted in the same spin channel.

In conclusions, the electronic structure near the Fermi level of Co-doped $PbPdO_2$ is shown clearly by the O K-edge XAS and PES spectra complemented with calculations of the electronic structure. O $2p$-Pd $4d$ hybridized bands contribute to the electronic structure near the Fermi level of Co-doped $PbPdO_2$, with an additional contribution of spin-polarized Co $3d$ states at a greater or smaller energy. The spin-polarized Co $3d$ states interact with the Pd $4d$ and O $2p$ hybridized states causing the spin splitting at band edge. The exchange interaction is based on the covalent hybridization

between Co $3d$-O $2p$ bands and Pd $4d$-O $2p$ bands. The spin-split band structure is essential for the intriguing physical properties of Co-doped $PbPdO_2$. High-temperature ferromagnetism arises as thermal excitation increases the carriers in the spin-split state of the conduction band with full spin polarization. Fully spin-polarized carriers are also expected to be obtained on precisely controlling the Fermi level across the spin-split states. The emission of fully circularly polarized light can also arise when the relaxation of the excited carriers is restricted in the same spin channel. This work exposes clearly the spin-split band structure of Co-doped $PbPdO_2$, contributing to a fundamental understanding of its magnetic characteristics and other physical properties. The understanding of how the electronic structure varies with chemical doping could also be the basis to design material systems, with desired electronic structures and spin polarization characteristics.

[1]H. van Leuken and R. A. de Groot, Phys. Rev. Lett. **74**, 1171 (1995).
[2]H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, and Y. Iye, Appl. Phys. Lett. **69**, 363 (1996).
[3]X. L. Wang, Phys. Rev. Lett. **100**, 156404 (2008).
[4]X. Wang, G. Peleckis, C. Zhang, H. Kimura, and S. Dou, Adv. Mater. **21**, 2196 (2009).
[5]S. W. Chen, S. C. Huang, G. Y. Guo, J. M. Lee, S. Chiang, W. C. Chen, Y. C. Liang, K. T. Lu, and J. M. Chen, Appl. Phys. Lett. **99**, 012103 (2011).
[6]K. J. Lee, S. M. Choo, J. B. Yoon, K. M. Song, Y. Saiga, C. Y. You, N. Hur, S. I. Lee, T. Takabatake, and M. H. Jung, J. Appl. Phys. **107**, 09C306 (2010).
[7]K. J. Lee, S. M. Choo, Y. Saiga, T. Takabatake, and M. H. Jung, J. Appl. Phys. **109**, 07C316 (2011).
[8]H. L. Su, S. Y. Huang, Y. F. Chiang, J. C. A. Huang, C. C. Kuo, Y. W. Du, Y. C. Wu, and R. Z. Zuo, Appl. Phys. Lett. **99**, 102508 (2011).
[9]Y. Pan and Z. Yang, Phys. Rev. B **82**, 195308 (2010).
[10]M. Tanaka, M. Hasegawa, T. Higuchi, T. Tsukamoto, Y. Tezuka, S. Shin, and H. Takei, Physica B **245**, 157 (1998).
[11]P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[12]G. Kresse and J. Hafner, Phys. Rev. B **48**, 13115 (1993).
[13]G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[14]P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).
[15]J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[16]S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B **57**, 1505 (1998).
[17]See supplementary material at http://dx.doi.org/10.1063/1.4768293 for details of experimental procedures and parameters of first principle calculations. The resonant PES spectra are also provided.
[18]K. Horiba, A. Chikamatsu, H. Kumigashira, and M. Oshima, Phys. Rev. B **71**, 155420 (2005).
[19]P. G. Steeneken, L. H. Tjeng, I. Elfimov, G. A. Sawatzky, G. Ghiringhelli, N. B. Brookes, and D.-J. Huang, Phys. Rev. Lett. **88**, 047201 (2002).
[20]S. Sanvito, P. Ordejon, and N. A. Hill, Phys. Rev. B **63**, 165206 (2001).
[21]J. M. D. Coey, J. Appl. Phys **91**, 8345 (2002).
[22]K. Ando, Science **312**, 1883 (2006).
[23]R. Chakarvorty, S. Shen, K. J. Yee, T. Wojtowicz, R. Jakiela, A. Barcz, X. Liu, J. K. Furdyna, and M. Dobrowolska, Appl. Phys. Lett. **91**, 171118 (2007).
[24]H. Akinaga, T. Manago, and M. Shirai, Jpn. J. Appl. Phys., Part 2 **39**, L1118 (2000).
[25]J. M. D. Coey, M. Venkatesan, and C. B. Fitzgerald, Nature Mater. **4**, 173 (2005).