Signature of Carrier-Induced Ferromagnetism in $Ti_{1-x}Co_xO_{2-\delta}$: Exchange Interaction between High-Spin Co^{2+} and the Ti 3*d* Conduction Band

J. W. Quilty,[1] A. Shibata,[2] J.-Y. Son,[1] K. Takubo,[3] T. Mizokawa,[1,3,2] H. Toyosaki,[4] T. Fukumura,[4] and M. Kawasaki[4,5]

[1]*PRESTO, Japan Science and Technology Corporation (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan*
[2]*Department of Complexity Science and Engineering, University of Tokyo, 5-1-5 Kashiwanoha, Chiba 277-8581, Japan*
[3]*Department of Physics, University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-0033, Japan*
[4]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[5]*Combinatorial Materials Exploration and Technology, Tsukuba 305-0044, Japan*

(Received 23 February 2005; published 17 January 2006)

X-ray photoemission spectroscopy measurements were performed on thin-film samples of rutile $Ti_{1-x}Co_xO_{2-\delta}$ to reveal the electronic structure. The Co 2*p* core-level spectra indicate that the Co ions take the high-spin Co^{2+} configuration, consistent with substitution on the Ti site. The high-spin state and the shift due to the exchange splitting of the conduction band suggest strong hybridization between carriers in the Ti 3*d* t_{2g} band and the t_{2g} states of the high-spin Co^{+2}. These observations support the argument that room temperature ferromagnetism in $Ti_{1-x}Co_xO_{2-\delta}$ is intrinsic.

DOI: 10.1103/PhysRevLett.96.027202 PACS numbers: 75.50.Pp, 71.22.+i, 73.20.At, 79.60.Dp

Reports of ferromagnetism at room temperature in anatase and rutile $Ti_{1-x}Co_xO_{2-\delta}$ [1,2] have attracted a considerable amount of attention [3–8]. If an intrinsic effect, this ubiquitous semiconductor would join the class of diluted magnetic semiconductors (DMS) which include colossal magnetoresistance and the anomalous Hall effect among their physical properties. That the maximum Curie temperature of known DMS materials is around 160 K [9] makes reports of room temperature ferromagnetism in a semiconductor particularly noteworthy. It has proved difficult, however, to determine whether the observed ferromagnetism is an intrinsic effect due solely to the substitution of Co on the Ti sites or an extrinsic effect due to the presence of clustered metallic Co.

Early reports of room temperature ferromagnetism in both anatase and rutile $Ti_{1-x}Co_xO_{2-\delta}$ were made by Matsumoto *et al.* [1,2]. The study of anatase combinatorial libraries [1] concluded that the Co ions occupy the Ti cation sites and that $Ti_{1-x}Co_xO_{2-\delta}$ can be viewed as a diluted magnetic (wide-gap) semiconductor. On the other hand, it has been claimed that the ferromagnetism is attributable to Co nanoclusters in the $Ti_{1-x}Co_xO_{2-\delta}$ thin films rather than the substituted Co ions [6,8]. The origin of ferromagnetism in both anatase and rutile $Ti_{1-x}Co_xO_{2-\delta}$ remains the subject of intense debate.

Very recently, anomalous Hall effect measurements on systematically produced rutile $Ti_{1-x}Co_xO_{2-\delta}$ films with different carrier doping levels [3] have confirmed room temperature ferromagnetism in this material, strongly suggesting that the ferromagnetism is intrinsic and not the result of Co clustering. At the same time as the anomalous Hall effect measurements were reported, a magnetization study of highly reduced rutile thin-film samples revealed the co-occurrence of superparamagnetism and anomalous Hall effect, casting doubt on the reliability of the anomalous Hall effect for determining whether ferromagnetism in $Ti_{1-x}Co_xO_{2-\delta}$ is intrinsic or extrinsic [8]. Determination of the effects of the Co impurity on the electronic structure and the electronic configuration of the Co impurity in $Ti_{1-x}Co_xO_{2-\delta}$ is thus very important for understanding the origins of the room temperature ferromagnetism in this potential DMS.

This Letter reports the results of x-ray photoemission spectroscopy (XPS) measurements of the electronic structure of rutile phase $Ti_{1-x}Co_xO_{2-\delta}$ thin films. These results show Co ions uniformly substituted on the Ti cation sites without detectable clustering, supporting the idea that the observed room temperature ferromagnetism is an intrinsic property of these films.

Rutile $Ti_{1-x}Co_xO_{2-\delta}$ thin films were taken from the same batches as the samples studied in Ref. [3], where room temperature ferromagnetism was observed. These films were deposited by laser molecular beam epitaxy on TiO_2-buffered sapphire substrates, with δ controlled by varying the oxygen partial pressure from 10^{-4}–10^{-8} torr [3]. This contrasts with the highly reduced films grown in high vacuum which show Co clustering [8]. Further details of sample fabrication may be found in Ref. [3]. A JEOL JPS-9200 spectrometer, with the Al $K\alpha$ line ($h\nu = 1486.6$ eV) as the x-ray source, was used to measure XPS spectra with an energy resolution of 0.6 eV under a base pressure of the order of 1×10^{-10} torr. Binding energies were calibrated to the Au 4*f* core-level peaks of a gold reference sample and the intensity of all spectra shown has been normalized by peak height unless otherwise stated. To remove the effects of band bending a Nd:YAG pulsed laser was used at an energy of 3.5 eV (355 nm) with frequency 30 Hz. The maximum incident energy density at the sample surface used was 200 $\mu J/cm^2$ per pulse and the effective pulse width was 6 ns.

$Ti_{1-x}Co_xO_{2-\delta}$ valence band spectra for $x = 0$, 0.01, 0.05, and 0.10 are shown in Fig. 1 and corresponding Co

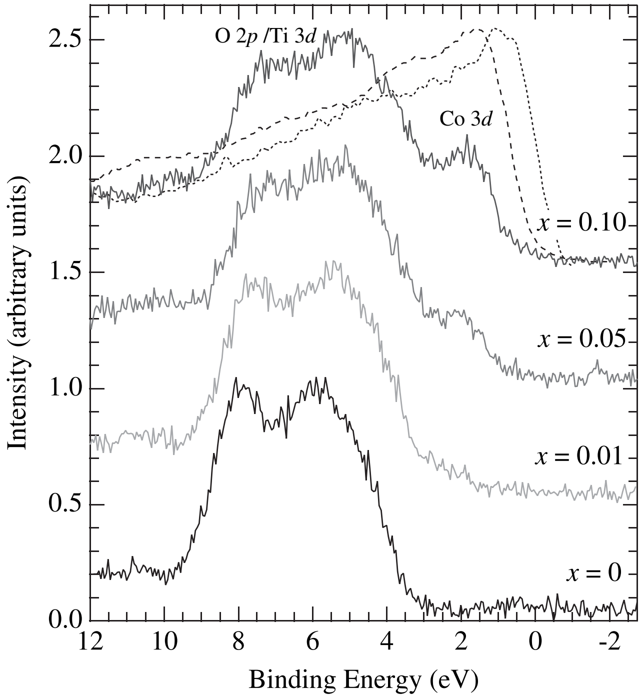

FIG. 1. Valence band x-ray photoemission spectra as a function of Co concentration x. Included for comparison are valence band spectra of metallic Co (dotted line) and CoO (dashed line) from Refs. [16,22].

$2p$ spectra are presented in Fig. 2. The pure TiO_2 valence band spectrum shows a band gap extending 3 eV below the Fermi level to the valence states which are derived from O $2p$ and Ti $3d$ [10]. Co substitution shifts the valence band to lower binding energy by up to 0.5 eV at $x = 0.10$ and causes a broad peak to appear in the spectra at around 2 eV, the intensity of which increases with Co concentration. The Co $2p$ core-level spectra exhibit a main Co $2p_{3/2}$ peak at 780.1 eV, accompanied by a relatively weak satellite peak around 786 eV, with the Co $2p_{1/2}$ peak appearing at 795.6 eV ($\Delta E = 15.5$ eV). There is little variation of the spectral line shapes and peak binding energies with Co concentration, showing that the local electronic structure of Co impurities in $Ti_{1-x}Co_xO_{2-\delta}$ is largely independent of x.

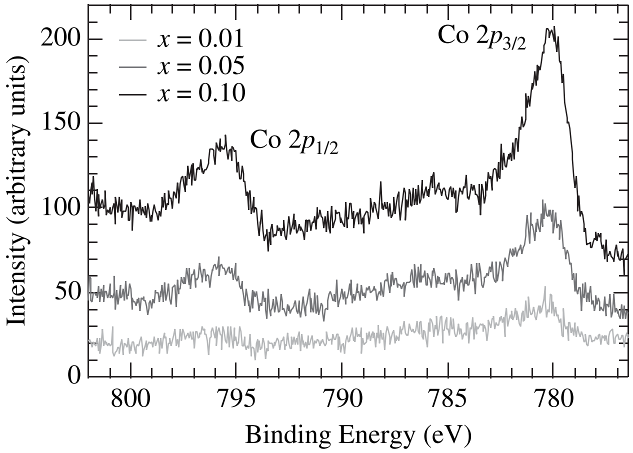

FIG. 2. Co $2p$ core-level x-ray photoemission spectra as a function of Co concentration x.

Both the Co $2p$ and valence band spectra show the signature of well-substituted Co ions at the film surface. First, the Co $2p_{3/2}$ binding energy, Co $2p_{3/2} - 2p_{1/2}$ separation, and satellite structure of the $Ti_{1-x}Co_xO_{2-\delta}$ spectra are significantly different from those of metallic Co and Co nanoclusters [11–13], which show Co $2p_{3/2}$ at 778.3–778.5 eV, $\Delta E = 15.0$ eV, and lack any satellite structure. Second, there is no discernible clustered metallic Co component in either the valence band (cf. the dotted line in Fig. 1) or Co $2p$ spectra, to an estimated detection threshold of 0.5 at. %. For the observed moment of just over $1\mu_B$/Co in the $x = 0.05$ and 0.10 films to be due to metallic Co clusters would require 65% of the total Co to cluster [14]. Such a large amount of clustered cobalt should be clearly visible in Figs. 1 and 2. Nevertheless, the possibility of a well-substituted surface with metallic Co clusters segregated to the bulk of the film cannot be categorically excluded by a surface-sensitive technique like XPS. The possibility of CoO at the film surface is excluded by the large differences in the valence band (cf. the dashed line in Fig. 1) and Co $2p$ line shapes. In particular, while the Co $2p$ main peak of CoO is wide due to lattice effects, that of $Ti_{1-x}Co_xO_{2-\delta}$ is rather narrow because the Co ions are isolated in $Ti_{1-x}Co_xO_{2-\delta}$.

The feature at 2 eV in Fig. 1 is indicative of the formation of an impurity band derived from the Co $3d$ orbitals and this observation implies that the donor level of the Co impurity is located just above the valence band maximum of TiO_2 in the dilute limit. These donor levels grow with Co doping and finally form the Co $3d$ impurity band. Although it is impossible to see the acceptor level using photoemission spectroscopy, the energy difference between the donor and acceptor levels is approximately given by the charge-transfer energy obtained from cluster model analysis of the Co $2p$ spectra. The Co impurity band is located 2 eV below the Fermi level for $x = 0.10$ and the entire band is shifted to lower binding energy by around 0.5 eV, as estimated later from Ti $2p$ and O $1s$ core-level spectra. The donor level is thus located 2.5 eV below the Fermi level in the dilute limit. As this value is comparable to the charge-transfer energy of 4 eV, it is expected that the acceptor level of the Co impurity is almost degenerate in energy with the conduction band minimum. In addition, since the TiO_6 octahedra are edge sharing in the rutile structure, direct hopping between the substituted Co $3d$ t_{2g} orbital and the neighboring Ti $3d$ t_{2g} orbital is expected to be large. These effects will enhance the exchange coupling between the Co $3d$ spins and the carriers in the Ti $3d$ conduction band [15].

Interstitial dopant substitution is a possibility in the rutile structure and to determine whether Co substitutes on the Ti site, rather than interstitially, it is necessary to determine the electronic state of the Co ion. Figure 3 shows a comparison of the measured Co $2p$ spectrum for $x = 0.10$ (dots) with the results of cluster model calculations (the solid line superimposed on the experimental data). An integral background has been added to the calculated spectrum. The cluster model calculations were performed for CoO_6 clusters and the best agreement with the measured spectrum was found for Co in the high-spin Co^{2+} state, with parameters $\Delta = 4.0$ eV, $U = 6.5$ eV, and $(pd\sigma) = -1.1$ eV. As interstitially substituted Co is predicted to take the low-spin state [5], the observation of a high-spin Co^{2+} state in the films indicates that the Co atoms are predominantly substituted on the Ti site.

Comparison with XPS spectra obtained from CoO, $LiCoO_2$, CoS_2, and $SrCoO_3$ [16–19], which exhibit a variety of Co electronic states, is also helpful. These spectra, with binding energies normalized at the Co $2p_{3/2}$ peak, are included in Fig. 3 and show high-spin Co^{2+} (CoO [16]), low-spin Co^{3+} ($LiCoO_2$ [16]), low-spin Co^{2+} (CoS_2 [18]), and low- or intermediate-spin Co^{4+} ($SrCoO_3$ [17,19]). The CoO spectrum shows the strongest resemblance to the $Ti_{1-x}Co_xO_{2-\delta}$ spectrum, arguing that the valence state of the Co cations in $Ti_{1-x}Co_xO_{2-\delta}$ is the divalent high-spin ground state seen in CoO [16]. This observation confirms the conclusions drawn from comparison of the rutile $Ti_{1-x}Co_xO_{2-\delta}$ spectrum with cluster model calculations.

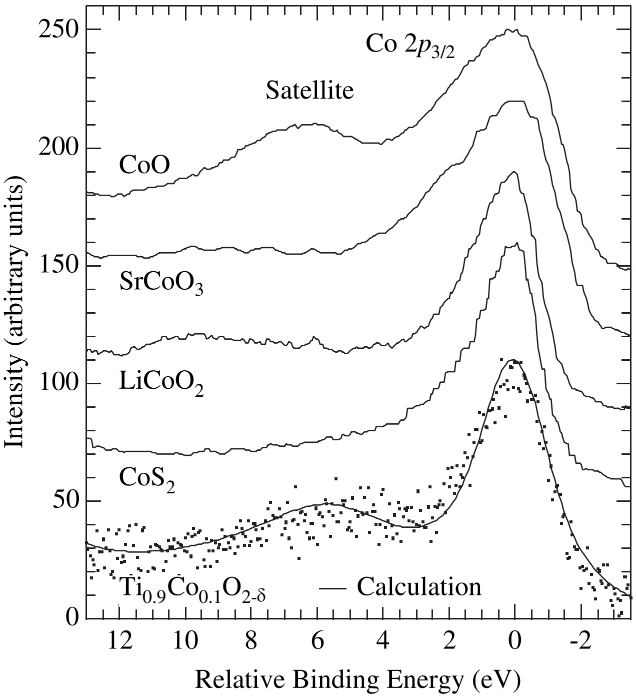

FIG. 3. Comparison of the Co $2p$ spectra from CoO [16], $SrCoO_3$ [17], $LiCoO_2$ [16], and CoS_2 [18] (solid lines) with that of $Ti_{0.9}Co_{0.1}O_{2-\delta}$ (dots). The solid line through the $Ti_{0.9}Co_{0.1}O_{2-\delta}$ spectrum shows the result of a cluster model calculation for CoO_6.

It is worth noting that while general agreement exists regarding the Co^{2+} oxidation state in both rutile and anatase $Ti_{1-x}Co_xO_{2-\delta}$, there is widespread disagreement over whether the spin state is high [4,6,20] or low [1,2,21]. Most conclusions of a low-spin state have been drawn from the low average magnetic moment observed in magnetization measurements. It may be difficult, however, to deduce the spin state from the magnetization due to the effects of disorder. For example, it has been suggested that interstitially substituted Co will strongly suppress the spin moment of the Co ions on the Ti site and thus the average Co magnetic moment [5].

The high-spin Co^{2+} state has a partially unoccupied t_{2g} orbital. This unoccupied Co $3d$ t_{2g} orbital is expected to strongly hybridize with the Ti $3d$ t_{2g} orbital, permitting direct t_{2g}-t_{2g} hopping as shown in Fig. 4. Such direct hopping should enhance the exchange coupling between the Co ions, increasing the magnetic moment [15]. Indeed, the rutile phase shows a higher average magnetic moment in magnetization measurements [3] compared to the anatase phase [1], consistent with this expectation.

Figure 5 shows Ti $2p$ and O $1s$ core-level spectra for all $Ti_{1-x}Co_xO_{2-\delta}$ films studied ($x = 0$, 0.01, 0.05, and 0.10). To remove the effect of band bending at the surface, the spectra were measured under laser irradiation at 3.5 eV. Photoexcitation is known to induce a surface photovoltage which cancels band bending at the surface. Consistent with this we observed a small increase in binding energy with photoexcitation in all samples, including pure TiO_2, signaling the removal of this extrinsic binding energy shift. The pure TiO_2 film shows a sharp, symmetric peak at a binding energy just under 530.4 eV, while the $x = 0.01$, 0.05, and 0.10 core-level peaks are somewhat broadened (particularly the $x = 0.10$ sample) and are shifted by 0.13, 0.18, and 0.50 eV to lower binding energy. This binding energy shift is attributed to a chemical potential shift due to the exchange splitting of the conduction band [3]. The impli-

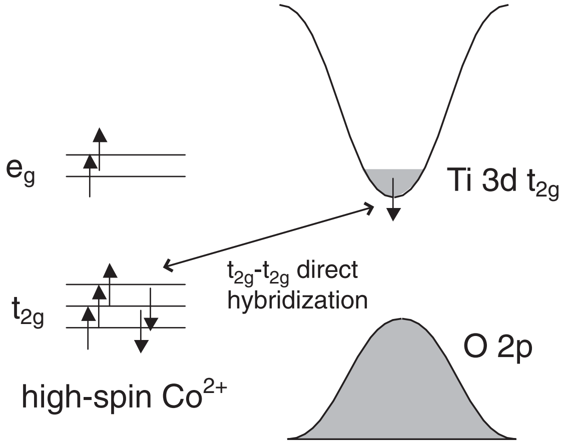

FIG. 4. Schematic band diagram showing the high-spin Co^{2+} state and the resulting strong t_{2g}-t_{2g} coupling between the Ti $3d$ and Co $3d$ t_{2g} states.

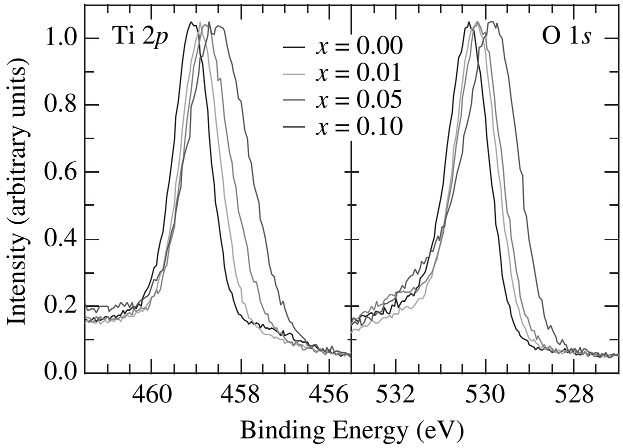

FIG. 5. Ti $2p$ and O $1s$ XPS core-level spectra as a function of cobalt doping showing the chemical potential shift. The energy shift due to band bending at the surface is removed by laser illumination.

cations of this binding energy shift—the degeneracy of the Co impurity acceptor level and the conduction band minimum—were discussed earlier.

In conclusion, we have studied the electronic structure of $Ti_{1-x}Co_xO_{2-\delta}$ ($x = 0.01$, 0.05, and 0.10) using x-ray photoemission spectroscopy. The electronic state of Co in rutile $Ti_{1-x}Co_xO_{2-\delta}$ is high-spin Co^{2+}, indicating substitution of the Co ions on the Ti sites. There is no discernible metallic Co signal in the XPS spectra. The valence band spectra show the evolution of a broad impurity band derived from the Co $3d$ orbitals located 2 eV below the Fermi level. A cluster model analysis of the Co $2p$ core-level spectrum gives a charge-transfer gap of 4 eV, while the magnitude of the exchange splitting of the conduction band is estimated to be as large as 0.5 eV from the residual Ti $2p$ and O $1s$ core-level binding energy shift relative to pure TiO_2. Taking into consideration the charge-transfer energy and the binding energy shift due to the exchange splitting, the acceptor level of the Co impurity is found to be almost degenerate in energy with the conduction band minimum. The degeneracy and direct t_{2g}-t_{2g} hopping, arising from hybridization between carriers in the Ti $3d$ t_{2g} band and the t_{2g} states of the high-spin Co^{2+}, are expected to enhance the exchange coupling between the carriers and the Co $3d$ spins and give the high Curie temperature observed in $Ti_{1-x}Co_xO_{2-\delta}$. These results are consistent with the view of rutile $Ti_{1-x}Co_xO_{2-\delta}$ as a diluted magnetic (wide-gap) semiconductor.

[1] Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Koshihara, and H. Koinuma, Science **291**, 854 (2001).
[2] Y. Matsumoto, R. Takahashi, M. Murakami, T. Koida, X.-J. Fan, T. Hasegawa, T. Fukumura, M. Kawasaki, S.-Y. Koshihara, and H. Koinuma, Jpn. J. Appl. Phys. **40**, L1204 (2001).
[3] H. Toyosaki, T. Fukumura, Y. Yamada, K. Nakajima, T. Chikyow, T. Hasegawa, H. Koinuma, and M. Kawasaki, Nat. Mater. **3**, 221 (2004).
[4] M. S. Park, S. K. Kwon, and B. I. Min, Phys. Rev. B **65**, 161201(R) (2002).
[5] W. T. Geng and K. S. Kim, Phys. Rev. B **68**, 125203 (2003).
[6] J.-Y. Kim *et al.*, Phys. Rev. Lett. **90**, 017401 (2003).
[7] S. R. Shinde *et al.*, Phys. Rev. B **67**, 115211 (2003).
[8] S. R. Shinde, S. B. Ogale, J. S. Higgins, H. Zheng, A. J. Millis, V. N. Kulkarni, R. Ramesh, R. L. Greene, and T. Venkatesan, Phys. Rev. Lett. **92**, 166601 (2004).
[9] D. Chiba, K. Takamura, F. Matsukura, and H. Ohno, Appl. Phys. Lett. **82**, 3020 (2003).
[10] J. C. Woicik, E. J. Nelson, L. Kronik, M. Jain, J. R. Chelikowsky, D. Heskett, L. E. Berman, and G. S. Herman, Phys. Rev. Lett. **89**, 077401 (2002).
[11] J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin-Elmer Corp., Eden Prairie, MN, 1992).
[12] E. Cattaruzza, F. Gonella, G. Mattei, P. Mazzoldi, D. Gatteschi, C. Sangregorio, M. Falconieri, G. Salvetti, and G. Battaglin, Appl. Phys. Lett. **73**, 1176 (1998).
[13] F. L. Wang, J. C. Jiang, and E. I. Meletis, J. Appl. Phys. **95**, 5069 (2004).
[14] Taking the average moment of metallic Co clusters to be the bulk value of $1.73\mu_B/\mathrm{Co}$.
[15] J. K. Furdyna, J. Appl. Phys. **53**, 7637 (1982).
[16] J. van Elp, J. L. Wieland, H. Eskes, P. Kuiper, G. A. Sawatzky, F. M. F. de Groot, and T. S. Turner, Phys. Rev. B **44**, 6090 (1991).
[17] T. Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano, Phys. Rev. B **56**, 1290 (1997).
[18] A. E. Bocquet, T. Mizokawa, T. Saitoh, H. Namatame, and A. Fujimori, Phys. Rev. B **46**, 3771 (1992).
[19] R. H. Potze, G. A. Sawatzky, and M. Abbate, Phys. Rev. B **51**, 11 501 (1995).
[20] H. Weng, X. Yang, J. Dong, H. Mizuseki, M. Kawasaki, and Y. Kawazoe, Phys. Rev. B **69**, 125219 (2004).
[21] X. F. Yao, T. J. Zhou, Y. X. Gai, T. C. Chong, and J. P. Wang, J. Appl. Phys. **95**, 7375 (2004).
[22] A. Galtayries and J. Grimblot, J. Electron Spectrosc. Relat. Phenom. **98–99**, 267 (1999).