Origin of the metallic conductivity in PdCoO$_2$ with delafossite structure

Masayuki Tanaka[a,*], Masashi Hasegawa[a], Thoru Higuchi[b], Takeyo Tsukamoto[b], Yasuhisa Tezuka[a], Shik Shin[a], Humihiko Takei[c]

[a] Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan
[b] Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan
[c] Graduate School of Science, Osaka University, Machikaneyama, Toyonaka-shi, Osaka 560, Japan

Abstract

Valence state, valence band structure and specific heat of metallic oxide PdCoO$_2$ with the delafossite structure, which has alternative layers of Pd, Co and O ions with a formation of each triangular lattice, are first investigated using polycrystalline samples by means of photoelectron spectroscopy and specific heat measurements. The lowest electrical resistivity in PdCoO$_2$ among the whole conductive oxides is attributable to a half-filled band formed by s–d hybrid orbitals originated from the monovalent Pd ions and coordinated oxygens. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

PdCoO$_2$ crystallizes in the delafossite-type structure which has alternative layers of Pd, Co and O ions, each of which forms an individual triangular lattice [1–3], as shown in Fig. 1. The name delafossite is derived from the mineral CuFeO$_2$. Co is in a distorted octahedral-site, coordinated with six oxygen atoms, and edge-shared octahedra form a CoO$_6$ layer, extended to the c-plane. On the other

hand, Pd is in a twofold, linear site, coordinated with two oxygen atoms, and oxygen is in a distorted tetrahedral-site, coordinated with three Co and one Pd atoms. Therefore, the delafossite structure can be recognized as a structure constructed by two-dimensional layers with the edge-linked CoO$_6$ octahedra connected by O–Pd–O dumbbells.

A lot of delafossite-type oxides have been reported. Most of them are mainly investigated in view of "frustrated magnetism" upon a two-dimensional triangular lattice. Detailed studies have been given on semiconducting CuFeO$_2$ [4, 5]. Among the delafossite oxides, however, there exist unique compounds showing metallic conductivity, such as

*Corresponding author. Tel.: 03 3478 6811(ext. 5722); fax: +81 03 3401 5169; e-mail: schenker@takeilab.issp.u-tokyo.ac.jp.
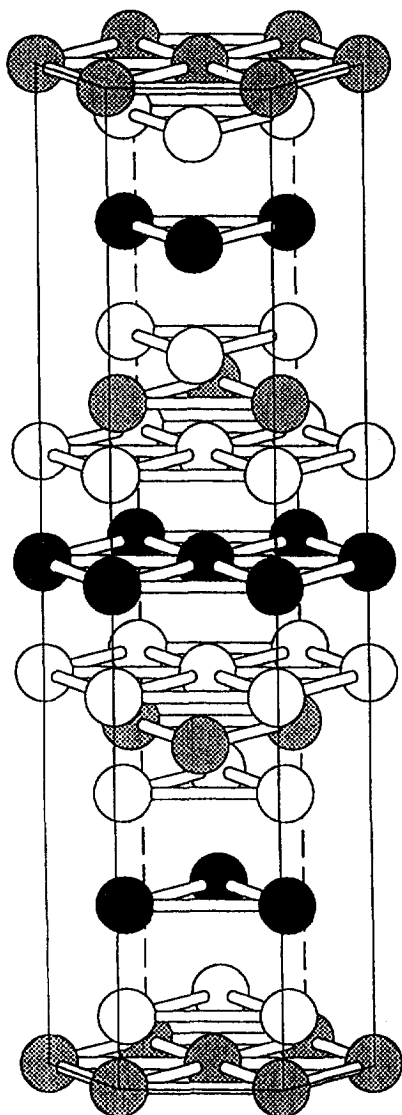
Fig. 1. Atom arrangement of PdCoO$_2$ in the delafossite-type structure. Closed, shaded and open circles indicate noble metal Pd, Co and O, respectively.

PdCrO$_2$, PdCoO$_2$, PdRhO$_2$ and PtCoO$_2$. Anisotropic temperature dependence of the electrical resistivity of PdCoO$_2$ single crystals was measured by our group [6]. PdCoO$_2$ showed very low resistivities in $\mu\Omega$ cm order perpendicular to the c-axis with large anisotropy and weakly temperature-dependent magnetic susceptibilities. The reported

value of the electrical resistivity is lowest in usual, normal-state oxides, the second lowest of which is 10 $\mu\Omega$ cm at room temperature in ReO$_3$ [7], and also lower than 11 $\mu\Omega$ cm of Pd metal at 270 K [8]. These metallic delafossites are also very anticipated in the field of crystal chemistry, since Pd or Pt is suggested to be located in the linear twofold site with unique monovalent state. It is very interesting to investigate the connection of such unique electronic state and the metallic conductivity of PdCoO$_2$.

In this study, the valence state, the valence band structure and the specific heat of PdCoO$_2$ is first investigated using powder samples. The origin of half-filled band will be discussed on the basis of our experimental data of the photoelectron spectroscopy and the specific heat, under the crystal-field theory.

2. Experimental details

PdCoO$_2$ in a crystalline form was obtained by the following metathetical reaction [1–3].

Pd + PdCl$_2$ + 2LiCoO$_2$ → 2PdCoO$_2$ + 2LiCl.
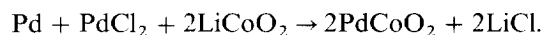
Mixtures of Pd, PdCl$_2$ and LiCoO$_2$ powders were weighed in accordance with the above reaction, and were enclosed in an evacuated silica tube. They were heated at 700°C for 40 h, and then cooled to room temperature. The crystalline products were well pulverized and washed by water so as to eliminate the resultant LiCl. Disk-shaped specimens, prepared by pressing the obtained powders, were embedded in the mixed powders of Pd, PdCl$_2$ and LiCoO$_2$, and sintered under the same condition as the above synthesis procedure.

Photoelectron spectroscopy measurements were performed at the photon factory (PF) in National Laboratory for High Energy Physics (KEK) by means of beam line BL-18A and 19B at the ultraviolet (UPS) and X-ray photoemission (XPS) regions, respectively. In the beam line, a constant deviation monochrometer and VG ESCALAB 500 photoelectron spectrometers are installed. The magnitude of the overall energy resolution of DECs was 90 meV at excitation energies ($h\nu$) of 60 eV, respectively. Measurement was performed under

10^{-11} torr using a polished surface of the sintered materials by filing. The Fermi energy was calibrated using the spectrum of Au 4f state.

The low-temperature specific heat (C) of polycrystalline $PdCoO_2$ sample was measured by a thermal relaxation method from 1.2 to 20 K [9, 10]. The sample was mounted on a bolometer together with a heater and a thermometer, and the assembly was contacted thermally with an outer system only by four thin copper wires.

3. Experimental results and discussion

3.1. Photoelectron spectroscopy

3.1.1. Valence state of $PdCoO_2$

X-ray absorption spectroscopy (XAS) was first performed to clarify the valence and spin states of Co. Fig. 2 shows the Co 2p XAS spectrum of $PdCoO_2$, which corresponds to the on-site transition $2p^6 3d^n \rightarrow 2p^5 3d^{n+1}$, where two groups of multiplets appear around 796 and 782 eV, corresponding to the $2p_{1/2}$ and $2p_{3/2}$ states, respectively. The obtained Co $2p_{3/2}$ XAS spectra in $PdCoO_2$ was compared with that of $LiCoO_2$ [11], and it has been established that the electronic state of Co in $LiCoO_2$ is the trivalent $(3d^6)$ ls state [12]. The profile of the main peak of $PdCoO_2$ around 782 eV is similar to that of $LiCoO_2$, whereas divalent Co shows a complex multiplet structure, which is characteristic of Co^{2+}. In the XAS spectra of $PdCoO_2$, a sub-peak is more clearly observed around 785 eV, which corresponds to the shoulder peak in $LiCoO_2$ around 784 eV. This spectrum shape is supported by a ligand-field multiplet (LFM) calculation of the $3d^6 \rightarrow 2p^5 3d^7$ transition assuming that Co is in the t_{2g}^6 ground state [13]. The Co 2p XAS spectra of $LaCoO_3$ and $LiCoO_2$ in the trivalent ls state of Co have been well reconstructed by use of the LFM calculation, as reported in Refs. [14, 15]. It is interesting to point out that the LFM calculation produces a clear sub-peak which is similar to the observed 785 eV peak in $PdCoO_2$. As stated in our previous paper [6], effective magnetic momentum was very small, suggesting that dominant Co are in trivalent ls state. In addition with our present Co 2p XAS and magnetic susceptibility measurements,
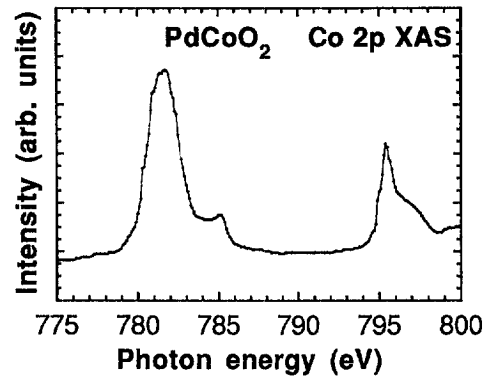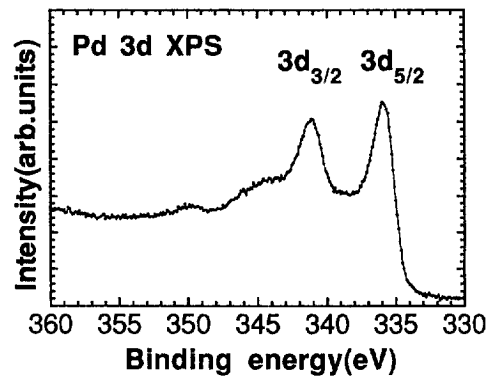

Fig. 2. Co 2p X-ray absorption spectrum of $PdCoO_2$.

Fig. 3. Pd 3d X-ray photoemission spectrum of $PdCoO_2$.

the electronic state of Co in $PdCoO_2$ is suggested to be in the trivalent ls state.

Fig. 3 shows the Pd 3d XPS spectra. There exist two groups of multiplets, corresponding to the $3d_{3/2}$ (339.0 eV) and $3d_{5/2}$ (335.8 eV) states. The $3d_{5/2}$ signal of Pd in $PdCoO_2$ appeared between that of metal Pd: 335.1 eV [16, 17] and PdO: 337.1 eV [18, 19], where it shifted to a more shallow level about 1.3 eV than that of the divalent $(4d^8)$ PdO. From the result of XAS where Co is in the trivalent ls state, the formal valence state of Pd is suggested to be monovalent $4d^9$. The observed chemical shift is consistent with the monovalent Pd in $PdCoO_2$ which is explained by the following simplified model [20]: deep levels in binding energy are ordinary expected from the atoms having less outer electrons as a result of

strong Coulomb interactions [21–25]. In conclusion, the results of Co 2p XAS with those of Pd 3d XPS spectra suggest that Pd is in the monovalent ($4d^9$) state.

3.1.2. Valence band structure

To investigate the valence band of $PdCoO_2$ more extensively, resonant photoemission experiments were performed near the Co 3p–3d resonant region. Resonant photoemission is a phenomenon of enhancement or suppression of photoemission due to a new emission channel of super-Coster–Kronig Auger decay. For $PdCoO_2$, the resonant photoemission involves two channels:

$$3p^6 3d^6 + h\nu \rightarrow 3p^6 3d^5 + e,$$

and

$$3p^6 3d^6 + h\nu \rightarrow 3p^5 3d^7 \rightarrow 3p^6 3d^5 + e.$$

The first channel is a direct photoemission channel, while the second channel, which will open when photon energy overcomes the 3p to 3d absorption threshold energy, is an Auger decay following a photoabsorption process. The final state of the two channels are indistinguishable because there is a quantum interference between the two channels. As a result of the interference, electrons in Co are enhanced or suppressed at the absorption threshold near 60 eV.

The valence band photoemissions as a function of the different photon energies – 61, 64, 70, 80 and 100 eV – are shown in Fig. 4, where peaks and shoulders designated A–D are apparent. Photon energy dependence of the cross sections of Co 3d, Pd 4d and O 2p are indicated in Ref. [26]. Above 50 eV, the cross sections of Co 3d and O 2p are decreasing with an increase in photon energy, whereas that of Pd 3d shows a minimum at 100 eV where photoemission is suppressed by a destructive interference between the initial and final states involved in the transition, named the Cooper minimum effect [27]. At photon energy of 100 eV where the main contribution to the UPS signal is Co 3d and O 2p, the peak A showed a narrow one at 1.5 eV whereas showed a slight shoulder at photon resonance energy of 61 eV. Peaks at the Fermi level can be assigned as the $3d^n\underline{L}$ charge
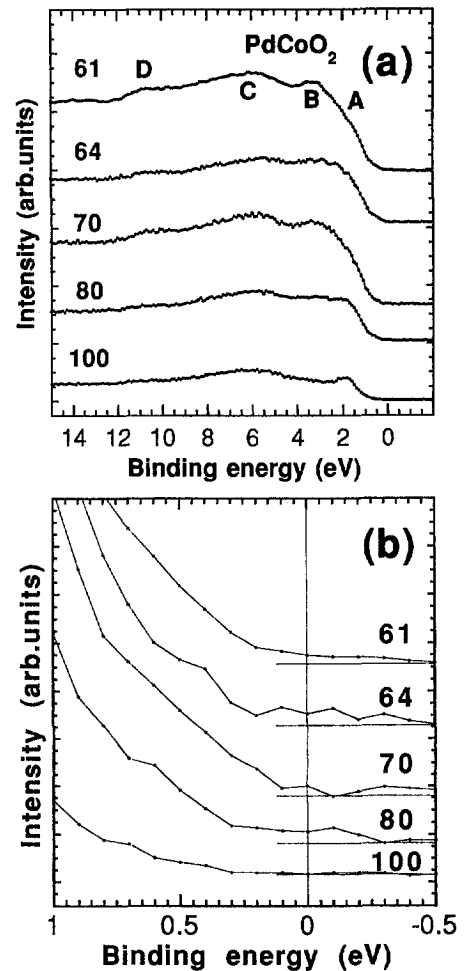

Fig. 4. (a) Photon-energy-dependent photoemission spectra of $PdCoO_2$ in the different photon energies, as indicated in the figure. (b) Enlarged patterns of photon-energy-dependent photoemission spectra of $PdCoO_2$ around the Fermi level, as indicated in the figure.

transfer state, whereas peaks that appeared at energies between 2 and 10 eV can be assigned as $3d^{n-1}$ state, showing much stronger resonance. These photon energy dependence were experimentally reported for most of the transition-metal oxides [28, 29] and the theoretical side of which were clearly explained by Tanaka and Jo [30]. It is interesting to measure and compare O 1s XAS spectrum in detail in order to clear the difference between $PdCoO_2$, and $LiCoO_2$ and CoO, etc. Results and discussion of them and comparison with

those of $LiCoO_2$ and CoO, etc. will be presented in our forthcoming paper.

To observe the density of states DOS at the Fermi energy E_F more exactly, an enlargement of the photon-dependent valence band spectra near E_F are performed, as shown in Fig. 4b. At 100 eV, DOS was considerably small and then it had a finite value with decreasing photon energies. As mentioned above, the cross section of Pd 4d shows the Cooper minimum at 100 eV. This indicates that Pd 4d mainly contributes to DOS at E_F.

3.2. Specific heat

Fig. 5 shows the result of specific heat measurement. In case of the $C/T - T^2$ relation, C/T was linearly decreasing with decreasing temperature and increasing below about 6 K. Fitting the formula $C = \gamma T + \beta T^3$ to the data above 6 K, the temperature coefficients γ and β were obtained as follows; $\gamma = 4.14$ (mJ/K^2 mol), and $\beta = 0.0822$ (mJ/K^4 mol). The Debye temperature Θ_D was obtained from β as 456 K. The observed divergence below 6 K is suggested to be due to unexpected magnetic impurities, but the XPD profiles showed no indication of such an impurity phase.

In order to consider the character of conduction electrons in $PdCoO_2$, the obtained value of γ was compared with those of various metals with s- or d-electrons. The metals with s-electrons – the alkali metals, such as Li (1.63), Na (1.38), K (2.08), Rb (2.41) and Cs (3.20) or the noble metals Cu (0.695),

Fig. 5. Specific heat C of $PdCoO_2$; $C/T - T^2$ relation.

Ag (0.646) and Au (0.729) – show values below 3.2, whereas those of d-electrons – V (9.26), Pd (9.42) or Pt (6.8) – lie over 6.8 [31]. The obtained γ value for $PdCoO_2$ locates at a middle between s- and d-metals.

4. Discussion on the origin of the metallic conductivity

4.1. Origin of the metallic conductivity in $PdCoO_2$

The formal valence state of Pd in $PdCoO_2$ was suggested to be monovalent $4d^9$ because Co is confirmed to be in a trivalent ls state from the results of the magnetic susceptibility [1–6] and the Co 2p XAS spectrum measurements. The Pd 3d XPS spectrum whose signal appeared in the region between metal Pd and divalent PdO, is also consistent with the above suggestion. Monovalent Pd has been first observed in the delafossite compound, as pointed out by Shannon et al. [1–3].

Since Pd is placed in a uniaxial crystalline field with the site symmetry $\bar{3}m$ in the delafossite structure, the fivefold degenerated 4d orbitals split into three levels [32]. The d_{z^2}-orbital with lobs extending toward the ligands takes the highest level, and the twofold, degenerated level of d_{xz} and d_{yz} with a z-axis component exists between the d_{z^2}-orbital and the twofold, degenerated lowest level of d_{xy} and $d_{x^2-y^2}$ where the c-axis is taken as the quantized z-axis. Such a uniaxial field can be obtained as a limit of the distorted octahedral field in case that four ligands on the x–y plane were infinitely kept away. The linear, twofold coordination is often observed in compounds including Cu^{1+}, Ag^{1+}, Au^{1+} or Hg^{2+} with fully occupied d^{10}-orbitals. Another limit is in the tetragonal, square-planar field without axial ligands, often observed in coordination compounds of Ni^{2+}, Pd^{2+} or Pt^{2+} with d^8, showing diamagnetism for the highly unstabilized $d_{x^2-y^2}$ orbital [33].

Orgel proposed a s–d hybridized orbitals model in order to explain the strong correlation of such an unique linear coordination and a d^{10} configuration [34, 35]. Since two energy levels of the 5s- and 4d-orbitals are known to be very close or the same, the unstabilized d_{z^2} orbital whose lobs extend
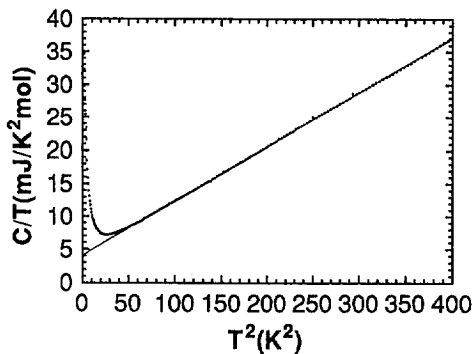
toward the ligands can hybridize with the empty 5s orbital as

$$\Psi_{d-s} = \frac{1}{\sqrt{2}}(d_{z^2} - s) \quad \text{and} \quad \Psi_{d+s} = \frac{1}{\sqrt{2}}(d_{z^2} + s).$$

Schematic drawings of these hybridized orbitals are shown in Fig. 6 [33, 34]. The Ψ_{d-s} orbital with concentrated electronic charge along the x–y plane is stabilized by benefit of the electrostatic energy.

In case of $PdCoO_2$ with the unique linear two-fold coordination, one electron occupies the highest d_{z^2} level because of monovalent Pd with $4d^9$. Under such a situation, the s–d hybridization also contributes to stabilize the system. If these half-filled s–d hybridized Ψ_{d-s} orbitals, extending along the c-plane, can overlap with each other, they form a half-filled conduction band. This Ψ_{d-s} orbital model leads to the idea that the lower metallic resistivity in $PdCoO_2$ than that in Pd metal is attributable to this s-character of the conduction band because of the well-known fact that Pd metal is a nearly ferromagnetic element, showing not only a considerably enhanced temperature-dependent paramagnetic behavior but also a broad maximum around 80 K by the strongest spin correlation of 4d electrons among 4d-metals [36–38].

From our experimental results, the 4d contribution on the Fermi level is clarified by the photon energy-dependent UPS study on the valence band. The specific heat measurement supports the s–d hybridized character of conduction electrons from
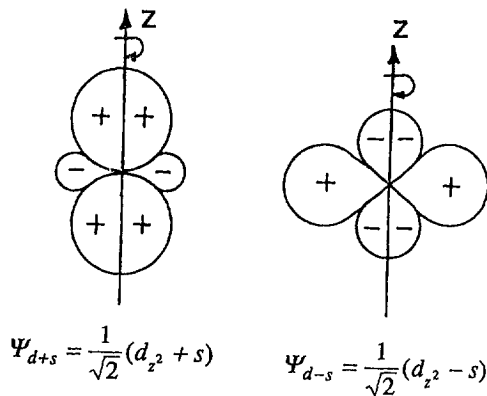
the value of the electronic specific heat coefficient γ to be 4.15, which is middle of the well-known s- and d-metals.

In conclusion, the metallic conductivity of $PdCoO_2$ is induced from the metallic bonds in the Pd plane. The half-filled conduction band is formed by overlapping of the s–d hybridized orbitals in connection with the twofold, linearly coordinated Pd with monovalent $4d^9$ in the delafossite structure.

4.2. Classification of metallic oxides by a difference in the Fermi energy and the position of $PdCoO_2$ among them

Metallic oxides can be classified into three categories as the d_ε, the d_γ and the s–p conductors by a difference in the Fermi energy in the conduction band [32]. It is apparent in the above classification that most of conductive oxides comprise the six-fold, octahedral coordination, yielding splitted d_ε and d_γ levels. Majority of them are known to be the d_ε conductor, since electrons are difficult to accommodate in the upper d_γ level by an increase in the crystal-field splitting from 3d, 4d to 5d. On the other hand, the d_γ conductor is quite rare and the high-temperature superconductive cuprates (HTSC) share the major part of them.

Let us discuss that $PdCoO_2$ corresponds to what kind of conductive oxide in the above classification. The s–p conductor is omitted from the selection, since the conduction band of $PdCoO_2$ is formed from the s–d hybridized orbitals. The minimum requirement of the d_ε (d_γ) conductor is to have less (more) than four hs or seven ls d electrons in a six-fold octahedral field. On the other hand, $PdCoO_2$ comprises the twofold, linear coordination but no Pd centered-octahedron. Therefore, the most reasonable way is to create a new, fourth group as the s–d conductor which presumably includes metallic delafossites such as $PdCrO_2$, $PdCoO_2$, $PdRhO_2$ and $PtCoO_2$. In such a s–d conductor, the hybridized s–d orbital is essential for constructing the conduction band, which is brought about by the half-filled s–d hybridized orbitals, originating from the monovalent Pd with $4d^9$ in a twofold, linear coordination in the delafossite structure.

Fig. 6. From the left to the right: the two s–d hybridized orbitals, $\Psi_{d+s} = \frac{1}{\sqrt{2}}(d_{z^2} + s)$ and $\Psi_{d+s} = \frac{1}{\sqrt{2}}(d_{z^2} - s)$, respectively [34, 35].

5. Conclusions

Physical properties of metallic oxide $PdCoO_2$ with the delafossite structure is first investigated by means of photoelectron spectroscopy and specific heat measurements. The present results lead to the conclusion that the metallic conductivity of $PdCoO_2$ is induced from the metallic bonded Pd plane, where the half-filled conduction band is constructed from the overlapping of the s–d hybridized orbitals, originating from the linear, twofold coordinated Pd in the monovalent $4d^9$ state. Thus, $PdCoO_2$ should be classified into the new category of the s–d conductor in the metallic oxides.

Acknowledgements

References

[1] R.D. Shannon, D.B. Rogers, C.T. Prewitt, Inorg. Chem. 10 (1971) 713.

[2] C.T. Prewitt, R.D. Shannon, D.B. Rogers, Inorg. Chem. 10 (1971) 719.

[3] D.B. Rogers, R.D. Shannon, C.T. Prewitt, J.L. Gillson, Inorg. Chem. 10 (1971) 723.

[4] S. Mitsuda, H. Yoshizawa, N. Yaguchi, M. Mekata, J. Phys. Soc. Japan 60 (1991) 1885.

[5] M. Mekata, N. Yaguchi, T. Takagi, T. Sugino, S. Mitsuda, H. Yoshizawa, T. Sugino, N. Hosoito, T. Shinjo, J. Phys. Soc. Japan 62 (1993) 4474.

[6] M. Tanaka, M. Hasegawa, H. Takei, J. Phys. Soc. Japan 65 (1996) 3973.

[7] T.P. Pearsall, C.A. Lee, Phys. Rev. B 10 (1974) 2190.

[8] Chemical Society of Japan (Ed.) Kagaku Binran, Maruzen, Tokyo, 1984, 3rd ed.

[9] R. Bachmann, F.J. DiSalvo Jr., T.H. Geballe, R.L. Greene, R.E. Howard, C.N. King, H.C. Kirsch, K.N. Lee, R.E. Schwall, H.-U. Thomas, R.B. Zubeck, Rev. Sci. Instrum. 43 (1972) 205.

[10] G.R. Stewart, Rev. Sci. Instrum. 54 (1) (1983) 1.

[11] J. van Elp, J.L. Wieland, H. Eskes, P. Kuiper, G.A. Sawatzky, F.M.F. de Groot, T.S. Turner, Phys. Rev. B 44 (1991) 6090.

[12] S. Kikkawa, S. Miyazaki, M. Koizumi, J. Solid State Chem. 62 (1986) 35.

[13] F.M.F. de Groot, J.C. Fuggle, B.T. Thole, G.A. Sawatzky, Phys. Rev. B 42 (1990) 5457.

[14] M. Abbate, J.C. Fuggle, A. Fujimori, L.H. Tjeng, C.T. Chen, R. Potze, G.A. Sawatzky, H. Eisaki, S. Uchida, Phys. Rev. B 47 (1993) 16124.

[15] F.M.F. de Groot, M. Abbate, J. van Elp, G.A. Sawatzky, Y.J. Ma, C.T. Chen, F. Sette, J. Phys.: Condens. Matter 5 (1993) 2277.

[16] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilenberg, Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer Co. Phys. Electronics Div., Minnesota, 1979.

[17] P. Weightman, P.T. Andrews, J. Phys. C. Sol. State Phys. 13 (1980) L815, L821.

[18] C. Furlani, G. Mattogno, J. Less-Common Met. 102 (1984) 89.

[19] I. Davoli, S. Stizza, A. Bianconi, M. Benfatto, C. Furlani, V. Sessa, Solid State Commun. 48 (1983) 475.

[20] S. Hüfner, Photoelectron Spectroscopy, Springer, Berlin, 1994.

[21] It is important to note here that some compounds were reported to show the shallower binding energy with increasing the valence state: L.N. Kramer, M.P. Klein, Chem. Phys. Lett. 8 (1971) 183.

[22] C.A. Tolman, W.M. Rigges, W.J. Linn, C.M. King, R.C. Wendt, Inorg. Chem. 12 (1973) 2770; J.C. Carver G.K. Schweitzer, T.A. Carlson, J. Chem. Phys. 57 (1972) 973.

[23] J.M. Thomas, M.J. Tricker, J. Chem. Soc. Faraday Trans. II 71 (1975) 329.

[24] I. Ikemoto, K. Ishii, S. Kinoshita, H. Kuroda, M.A. Alario Franko, J.M. Thomas, J. Solid State Chem. 17 (1976) 425.

[25] P.A. Grutsch, M.V. Zeller, T.P. Fehlner, Inorg. Chem. 12 (1973) 1431.

[26] J.J. Yeh, I. Lindau, At. Data Nucl. Data Tables 32 (1985) 1.

[27] J.W. Cooper, Phys. Rev. 128 (1962) 681.

[28] S.J. Oh, J.W. Allen, I. Lindau, J.C. Mikkelsen Jr., Phys. Rev. B 26 (1982) 4845.

[29] Z.X. Shen, J.W. Allen, J.J. Yeh, J.S. Kang, W. Ellis, W.E. Spicer, I. Lindau, M.B. Maple, Y.D. Dalichaouch, M.S. Torikachvili, J.Z. Sun, T.H. Geballe, Phys. Rev. B 36 (1987) 8414.

[30] A. Tanaka, T. Jo, J. Phys. Soc. Japan. 63 (1994) 2788.

[31] C. Kittel, Introduction to Solid State Physics, 6th ed. Wiley, New York, 1986.

[32] H. Kamimura, S. Sugano, Y. Tanabe, Ligand Field Theory and Its Applications, Syokabo, Tokyo, 1969.

[33] F.A. Cotton, G. Wilkinson, P.L. Gauss, Basic Inorganic Chemistry. Wiley, New York, 1987.

[34] L.E. Orgel, J. Chem. Soc. (1958) 4186.

[35] L.E. Orgel, An Introduction to Transition-Metal Chemistry: Ligand-Field Theory, Wiley, New York, 1960.

[36] D.W. Budworth, F.E. Hoare, J. Preston, Proc. Roy. Soc. A 257 (1960) 250.

[37] A.J. Manuel, J.M.P. st Quinton, Proc. Roy. Soc. A 273 (1963) 412.

[38] M. Takigawa, H. Yasuoka, J. Phys. Soc. Japan. 51 (1982) 787.