PHYSICAL REVIEW B **73**, 094426 (2006)

X-ray absorption near-edge spectroscopy study of Mn and Co valence states in $LaMn_{1-x}Co_xO_3$ ($x=0-1$)

M. Sikora,[1,2] Cz. Kapusta,[1] K. Knížek,[3] Z. Jirák,[3] C. Autret,[3] M. Borowiec,[1] C. J. Oates,[1] V. Procházka,[1,4]
D. Rybicki,[1] and D. Zajac[1]

[1]*Solid State Physics Department, Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Av. Mickiewicza 30, 30-059 Cracow, Poland*
[2]*European Synchrotron Radiation Facility, BP 220, 38043 Grenoble Cedex, France*
[3]*Institute of Physics, Cukrovarnická 10, 162 53 Prague 6, Czech Republic*
[4]*Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, 180 00 Prague 8, Czech Republic*

(Received 24 November 2004; revised manuscript received 14 February 2006; published 21 March 2006)

A systematic study of the valence states of Mn and Co in the perovskite series $LaMn_{1-x}Co_xO_3$ ($x=0$ to 1) by means of x-ray absorption near edge spectroscopy (XANES) at the K-edges is presented. The chemical shift and the evolution of the pre-edge features reveal a gradual increase of the average oxidation level of both, Mn and Co ions, with Co doping, which suggests that mixed valence states of Co^{2+}/Co^{3+} and Mn^{3+}/Mn^{4+} exist in the whole solid solution range. The relation of the results to the magnetic properties of the compounds is discussed.

DOI: 10.1103/PhysRevB.73.094426 PACS number(s): 75.50.Cc, 72.80.Ga, 78.70.Dm

INTRODUCTION

The solid solution system $LaMn_{1-x}Co_xO_3$ has recently attracted much attention owing to ferromagnetic (FM) interactions dominating for intermediate values of x. These give rise to ferromagnetic and cluster glass ground states with $T_C=140-240$ K (Ref. 1), which is in contrast with the behavior of the end members that are either antiferromagnetic, $LaMnO_3$, or diamagnetic, $LaCoO_3$. The occurrence of ferromagnetism provoked a discussion about its origin, which has always been closely related to the question on the Mn and Co valence. Goodenough[2] interpreted the FM interactions in the intermediate region as a consequence of dynamic Jahn-Teller effect of octahedrally coordinated Mn^{3+} ions, giving rise to positive super-exchange interactions Mn^{3+}-O-Mn^{3+}. However, this does not agree with the concept of charge disproportionation of trivalent transition metals cations into Co^{2+} and Mn^{4+}, which was proposed by Blasse for $x=0.5$, based on an analysis of magnetic susceptibility.[3] The FM interactions were attributed to superexchange interactions between Co^{2+}-O-Mn^{4+}. A systematic study of the magnetic and transport properties of $LaMn_{1-x}Co_xO_3$ system was performed by Troyanchuk.[1] In this work the magnetic properties of $LaMn_{1-x}Co_xO_3$ were discussed in terms of competition between the ferromagnetic Mn^{3+}-O-Mn^{4+}, Mn^{3+}-O-Mn^{3+}, Co^{2+}-O-Mn^{4+} and antiferromagnetic Mn^{4+}-O-Mn^{4+}, Co^{2+}-O-Co^{2+}, Mn^{3+}-O-Co^{2+} superexchange interactions, considering also a tendency to Co^{2+}/Mn^{4+} ionic ordering of the NaCl type.

In order to resolve the question on the Mn and Co valence states in $LaMn_{1-x}Co_xO_3$ perovskites, several x-ray absorption spectroscopy measurements in the near-edge region (XANES) were undertaken. Park[4] determined a rigid valence state Co^{2+} and mixed valence Mn^{3+}/Mn^{4+} from spectra at the $L_{2,3}$-edges for $x=0.15$, and rejected the possibility of a mixed valence Co^{2+}/Co^{3+}. The FM interactions were attributed to the double exchange between Mn^{3+} and Mn^{4+}. The presence of the Co^{2+} valence state was deduced from the XANES measurements at Co and Mn K-edges on samples with smaller level of doping ($x\leqslant 0.10$) by Toulemonde.[5] On the other hand, van Elp,[6] in response to Park's work, argued for mixed Co^{2+}/Co^{3+} valence state by a comparison to XANES spectra at Co $L_{2,3}$ edges of $Li_xCo_{1-x}O$ oxides. In summary, all the earlier XANES results suggest a charge redistribution $Co^{3+}+Mn^{3+}\leftrightarrow Co^{2+}+Mn^{4+}$, however, there is controversy about its actual extent. The aim of our present work is a systematic study of the whole series $LaMn_{1-x}Co_xO_3$.

XANES is an element selective technique, which has successfully been utilized to study local valence states of transition metals (TM) in colossal magnetoresistive manganites and other strongly correlated oxides.[5,7–13] The TM K-edge corresponds to a dipole transition of a $1s$ core electron into the p-like unoccupied states. Since the $4p$ states of transition metals are strongly hybridized with O $2p$ and TM $3d$ states of the neighboring atoms, the local p-like density of states is very sensitive to the charge distribution and local distortions of TM-O bonds, as well as to any variations in TM $3d$-O $2p$ hybridization that is believed to affect the electronic states near the Fermi energy.[14,15] Moreover, the K-edge spectra of transition metals reveal pre-edge structures, which are ascribed to quadrupole $1s$-$3d$ and/or to modifications of dipole transition probability due to hybridization between $3d$ and $4p$ states. Although the origin of the pre-edge structures is still a matter of controversy,[16,17] their spectral shape can be used as a direct probe of the $3d$ band modification and, thus, the valence evolution.[18]

EXPERIMENTAL

The $LaMn_{1-x}Co_xO_3$ samples were prepared by solid state reaction at high temperature. Homogenized mixtures of appropriate oxides and carbonates were calcined at 900 °C to achieve decarbonation. The pre-reacted powder was pressed in the form of pellets, which were shortly heated in air to

1500 °C (1 h duration), sintered at 1300 °C for 40 h and slowly cooled down to the room temperature. Since the Mn-rich compounds ($x \leqslant 0.4$) were showing an excess of oxygen after sintering in air, they were annealed afterwards at 1100 °C under vacuum of 10^{-3} mbar for two days. Powder x-ray diffraction (Bruker D8, Cu $K\alpha$) confirmed the formation of single-phase compounds. The symmetry of the phases is orthorhombic *Pbnm* for $x \leqslant 0.6$ and rhombohedral $R\bar{3}c$ for $x \geqslant 0.6$. The structural, magnetic, and transport properties over a wide temperature range 10–900 K are reported elsewhere.[19] The oxygen stoichiometry δ of the $LaMn_{1-x}Co_xO_{3+\delta}$ compounds was estimated by comparing lattice parameters with reference data. The comparison shows, that $x=0$ compound is slightly overstoichiometric ($\delta=0.02$), whereas $x=1$ compound is stoichiometric ($\delta=0$), see Ref. 19 for details.

The Mn and Co K-edge XANES spectra were collected at the A1 beamline of Hasylab/DESY Synchrotron Laboratory in Hamburg, Germany, using a high resolution four Si(111) crystal monochromator. The absorption spectra were recorded at room temperature on powder samples of $LaMnO_3$, $LaMn_{1-x}Co_xO_3$ with $x=0.2$, 0.4, 0.5, 0.6, 0.8, and $LaCoO_3$. Four spectra for each sample and edge were measured using transmission mode with simultaneous measurement of one reference sample from the set of $MnCO_3$ (Mn^{2+}), Mn_2O_3 (Mn^{3+}), $CaMnO_3$ (Mn^{4+}), $Co(NO_3)_2$ (Co^{2+}), and Co_2O_3 (Co^{3+}). The higher-order harmonics were suppressed by detuning the fourth crystal of the monochromator on its rocking curve to 60% of the maximum transmitted intensity at 200 eV above the edge. Afterwards, all the spectra were put onto the same relative scale and the absolute energy was calibrated by assigning the energy of 6539 eV to the first inflection point of the pure Mn foil and 6555 eV to the main peak of Mn_2O_3 spectra. The energy scale at the Co K-edge was calibrated by assigning the value of 7725.9 eV to the main peak of the $LaCoO_3$ spectrum.[20] Possible errors arising from shifts of the energy scale between individual spectra were minimized by a careful comparison of their first derivative with those of the reference spectra. The relative shifts of reference spectra were not larger than 150 meV,[21] which is below the monochromator resolution and the core hole lifetime broadening—estimated at 0.6 and 0.7 eV for the Mn and Co K-edge, respectively. After the energy calibration all the spectra were normalized by setting the edge step to unity and, eventually, the appropriate spectra were averaged. The quantitative information on the pre-edge peak intensity and the edge energy was obtained using a deconvolution procedure similar to that described by Hass *et al.*[20]

RESULTS AND DISCUSSION

The edge normalized XANES spectra at the Mn K-edges of $LaMn_{1-x}Co_xO_3$ series as well as $MnCO_3$, $LaMnO_3$, and $CaMnO_3$ references are presented in Fig. 1. Their shapes are similar for all the compounds studied, exhibiting a structured pre-edge region and the dominant peak (white line), which gradually shifts towards higher energy with increasing Co content. The pre-edge region reveals three distinct features. The two appearing at the energies of ~6539 eV (A_1) and ~6541 eV (A_2), reveal small shift towards higher energies with Co doping (inset of Fig. 1). We ascribe them to the empty majority and minority $3d$ electronic states, respectively.[15] Their splitting of order of 2 eV is consistent with that observed in $La_{1-y}Ca_yMnO_3$ series by Bridges *et al.*[18] The third pre-edge feature, observed in the energy range of 6543–6547 eV, reveals much stronger energy shift, similar to that of the white line. This behavior indicates that this feature originates from intra-atomic $1s$-$4p$ dipole transitions.[15]

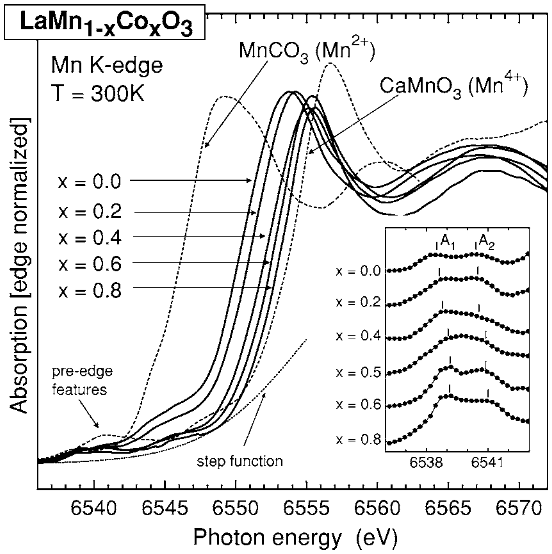

FIG. 1. Normalized XANES spectra at Mn K-edges of the $LaMn_{1-x}Co_xO_3$ series together with those of $MnCO_3$, $LaMnO_3$ ($x=0$) and $CaMnO_3$ for reference. The $LaMn_{0.5}Co_{0.5}O_3$ spectrum is omitted for clarity. The inset shows a comparison of the pre-edge A_1 and A_2 features after subtraction of the edge step function.

The white line of the Mn K-edge consists of a single peak in the energy range of 6553–6556 eV which gradually shifts towards higher energy with increasing Co content. A similar systematic shift of this peak with the change of valence has been established in experimental studies of the related perovskite systems, $La_{1-y}Ca_yMnO_3$ (Refs. 8 and 9), $LaNi_{1-y}Mn_yO_{3+\delta}$ (Ref. 22) and $LaMn_{1-y}Ga_yO_3$ (Ref. 23), and supported by recent *ab initio* electronic structure calculations on embedded octahedral MnO_6 clusters.[24] In the present series the energy shift is observed, both in the edge position, taken as the inflection point of the absorption edge, as well as in the main peak position. For all of the $x>0$ spectra the edge energy is intermediate between those of $CaMnO_3$ and $LaMnO_3$ and is gradually changing with Co doping. The latter result suggests that the average valence state of manganese increases with Co doping from Mn^{3+} towards Mn^{4+}. Also the gradual increase of the intensity of A_1pre-edge features and a small, but resolved, decrease of the (exchange) splitting of the A_1 and A_2 features, from 2.2 eV for $x=0$ to 1.8 eV for $x=0.8$, are consistent with this finding.[18]

In addition, the Co K-edge XANES spectra (Fig. 2) reveal a systematic increase of the edge and the main peak energies with cobalt doping. The pre-edge structures at Co K-edges are less pronounced and consist of two features in the energy

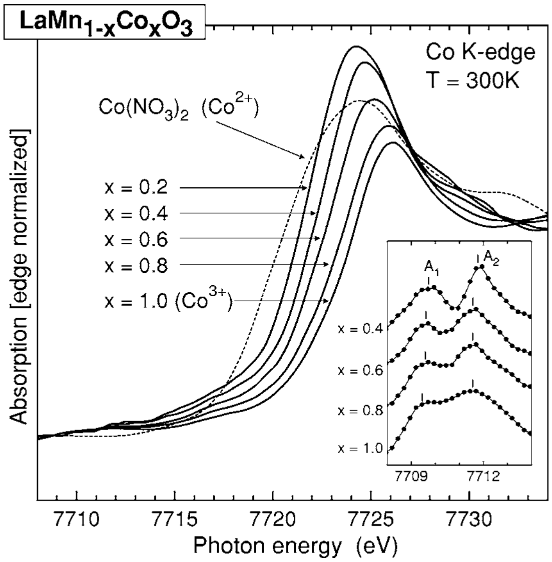

FIG. 2. Normalized XANES spectra at Co K-edges of $LaMn_{1-x}Co_xO_3$ series, together with those of $Co(NO_3)_2$ and $LaCoO_3$ ($x=1$) for reference. The spectrum of $LaMn_{0.5}Co_{0.5}O_3$ is omitted for better clarity. The inset shows a comparison of the pre-edge A_1 and A_2 features after subtraction of the edge function.

range of 7709–7712 eV, denoted as A_1 and A_2 in the inset of Fig. 2. Following the analysis of Hass *et al.*[20] we ascribe them to the quadrupole $1s$-$3d$ transitions into unoccupied t_{2g} and e_g minority states. They show a splitting of order of 2.3 eV, similarly to the pre-edge features in the Mn K-edge spectra. A small shift of their positions by ~0.3 eV towards lower energies upon Co doping is observed, in contrast to the pre-edge features in the Mn K-edge spectra, where a shift towards higher energies was found. The pre-edge region in all the compounds studied reveals another two features at the energies of 7716 and 7722 eV, independent on the Co content, which possibly originate from ligand-to-metal charge transfer and $1s$-$4sp$ hybrid transition, respectively, as it was widely discussed for $LaCoO_3$ by Hass *et al.*[19] The main edge energy for all the solid solutions of $LaMn_{1-x}Co_xO_3$ is intermediate between those of $Co(NO_3)_2$ and $LaCoO_3$ and increases gradually with increasing x. This suggests that the average valence state shifts towards Co^{3+} with increasing cobalt content. The same conclusion can be drawn from the gradual increase of the intensity of the A_2 pre-edge structure.

The analysis of the Mn and Co K-edge shifts was performed using edge energies of the $MnCO_3$, $CaMnO_3$, $Co(NO_3)_2$ and $LaCoO_3$ reference samples as standards of the formal valence states: Mn^{2+}, Mn^{4+}, Co^{2+}, and Co^{3+}, respectively. Assuming a linear dependence of the chemical shift on the average valence,[8,22–24] one can obtain quantitative information on the valence state in the doped compounds. A preliminary test performed on the $LaMnO_3$ sample showed $Mn^{3.05+}$ as an average valence state, which is in good agreement with the oxygen stoichiometry analysis of this sample.[19] The average valence states derived for the other members of the $LaMn_{1-x}Co_xO_3$ series are presented in the Table I.

TABLE I. Transition metal ions K-edge position and average valence state in the compounds studied. "TM valence" is an x-weighted average of the Co and Mn average valence states, which suppose to be equal to 3.00 in the case of perfect oxygen stoichiometry. The uncertainty of the valence states presented is estimated to 0.05 of elementary charge per atom.

Sample	Mn K-edge (eV)	Mn valence	Co K-edge (eV)	Co valence	TM valence
$LaMnO_{3.02}$	6551.1	3.05			3.05
$LaMn_{0.8}Co_{0.2}O_3$	6551.7	3.18	7722.0	2.30	3.00
$LaMn_{0.6}Co_{0.4}O_3$	6552.4	3.34	7722.8	2.53	3.02
$LaMn_{0.5}Co_{0.5}O_3$	6552.8	3.46	7723.0	2.60	3.03
$LaMn_{0.4}Co_{0.6}O_3$	6553.1	3.52	7723.4	2.71	3.03
$LaMn_{0.2}Co_{0.8}O_3$	6553.6	3.64	7724.0	2.88	3.03
$LaCoO_3$			7724.4	3.00	3.00

In order to distinguish between the two possibilities for a coexistence of different valence states, i.e., localized or fluctuating between two formal states, the spectra of doped compounds were compared with weighted averages of the appropriate reference spectra. Figure 3 shows such a comparison at the Mn K edges for $x=0.2$, 0.5, and 0.8. The weighted spectra reproduce very well the edge energy, whereas they fail to reproduce the intensity and the shape of the white line. In all the cases the edge slope of the experimental spectrum is steeper than that of the weighted one. These results are strongly in favor of an intermediate valence state of Mn, which can be related to double-exchange-like valence fluctuations.[9,18,22] The presence of the double exchange driven intermediate valence state Mn^{3+}/Mn^{4+} has also been detected in the preliminary NMR measurements on the

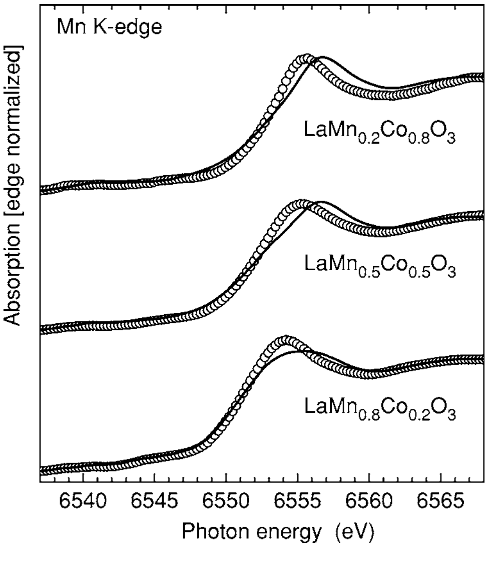

FIG. 3. A comparison of the experimental spectra (open circles) and the weighted average of the reference spectra (solid lines) at the Mn K-edges for the low, intermediate, and heavy doped samples.

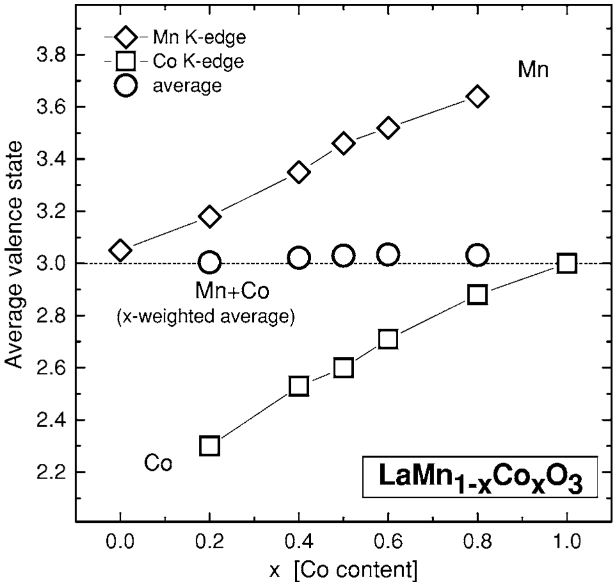

FIG. 4. The evolution of the average valence state of Mn (open diamonds) and Co (open squares) ions in the $LaMn_{1-x}Co_xO_3$ series derived from the Mn and Co K-edge shifts (lines are guides for eyes). Open circles represent the x-weighted average valence states of the $3d$ transition metal (B site), which are close to 3+ (dotted line) for all the compounds studied.

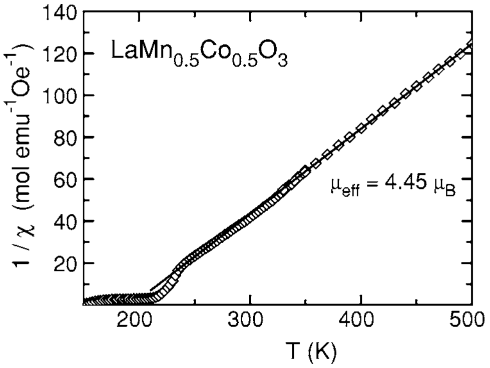

FIG. 5. Temperature dependence of the inverse magnetic susceptibility of $LaMn_{0.5}Co_{0.5}O_3$.

sample with $x=0.5$.[25] As to the Co^{2+}/Co^{3+} coexistence in the doped samples, the steep slope and systematic shift of the Co K edges in Fig. 2 suggest that intermediate valence is also inherent to cobalt sub-system rather than charge disproportionation.

The evolution of both Co and Mn valences is almost linear with x, as can be seen in Fig. 4. The weighted valence state of transition metal ions is equal to 3+ within the experimental error margin, indicating a good oxygen stoichiometry of the samples. Assuming a linear extrapolation of the Co and Mn valences against x, we estimated the extrapolated valence $Co^{2.15+}$ for $x \rightarrow 0$ and $Mn^{3.8+}$ for $x \rightarrow 1$. This indicates that even for a finite substitutions the intermediate valence states of dopants, Mn^{3+}/Mn^{4+} in $LaCoO_3$ and Co^{2+}/Co^{3+} in $LaMnO_3$, should be considered, which supports the valence fluctuations scenario.

Consistently with previous indications, the present study shows with much more precision that cobalt enters $LaMnO_3$ already in the mixed valence state Co^{2+}/Co^{3+}, introducing ~0.85 of an itinerant hole (Mn^{4+}) into the Mn^{3+} array. Conversely, for the other end member, $LaCoO_3$, the Mn ions enters in a mixed state of Mn^{3+}/Mn^{4+}, inducing high-spin Co^{2+} species ($S=1.5$) into the matrix of Co^{3+} ions.

A more complex situation occurs at the intermediate compositions, in particular for $x \sim 0.5$, where the XANES results reveal intermediate valence states $Co^{2.60+}$ and $Mn^{3.46+}$ (see Table I). The inverse susceptibility measured on the same sample shows a linear Curie-Weiss behavior above $T_C=210$ K,[19] corresponding to the effective moment $\mu_{eff}=4.45\mu_B$, see Fig. 5. The experimental μ_{eff} is in an excellent agreement with the theoretical value $\mu_{theor}=4.46\mu_B$ expected for a 50:50 mixture of $Co^{2.60+}$ in HS state ($S=1.8$) and $Mn^{3.46+}$ in HS state ($S=1.77$). The charge disproportionation model with $Co^{3+/2+}$ (60:40) in HS states and $Mn^{3+/4+}$ in HS states (54:46), which gives 43% of spins $S=1.5$ ($Co^{2+}+Mn^{4+}$) and 57% of $S=2$ ($Co^{3+}+Mn^{3+}$), results in slightly higher value $\mu_{theor}=4.49\mu_B$, however, the difference between the two μ_{theor} is comparable with experimental errors. Nevertheless, the analysis of susceptibility in the view of XANES results suggests that $Co^{2+/3+}$ is in the high spin state at intermediate x.

CONCLUSIONS

The Mn and Co valence states in the $LaMn_{1-x}Co_xO_3$ solid solutions have been investigated by an element selective technique of x-ray absorption spectroscopy in the near edge range. A systematic evolution of XANES spectra with x has been observed at the transition metal K-edges, which shows that the Mn and Co valences vary almost linearly with cobalt doping. A comparison of the spectra of doped compounds with weighted average of reference spectra suggests that the mixed-valent ions form two interpenetrating sub-systems (Co^{2+}/Co^{3+} and Mn^{3+}/Mn^{4+}) rather than stable pairs Co^{2+} $+Mn^{4+}$ coexisting with surplus Mn^{3+} or Co^{3+}. A quantitative comparison of the derived average valence states to the magnetic properties of the compounds reveals that at intermediate values of x the transition metal ions are in their high spin states.

ACKNOWLEDGMENTS

We thank E. Welter (Hasylab) for his kind assistance during x-ray absorption experiments. Work was performed within the frames of the EU RTN SCOOTMO, Project No. HPRN-CT-2002-00293. Partial support by the State Committee for Scientific Research, Poland and by the European Community - Research Infrastructure Action under the FP6 "Structuring the European Research Area" Programme (through the Integrated Infrastructure Initiative "Integrating Activity on Synchrotron and Free Electron Laser Science") is acknowledged. Part of the work was supported by the Project No. 202/06/0051 of the Grant Agency of the Czech Republic.

[1] I. O. Troyanchuk, L. S. Lobanovsky, D. D. Khalyavin, S. N. Pastushonok, and H. Szymczak, J. Magn. Magn. Mater. **210**, 63 (2000).

[2] J. B. Goodenough, A. Wold, R. J. Arnott, and N. Menyuk, Phys. Rev. **124**, 373 (1961).

[3] G. Blasse, J. Phys. Chem. Solids **26**, 1969 (1965).

[4] J.-H. Park, S.-W. Cheong, and C. T. Chen, Phys. Rev. B **55**, 11072 (1997).

[5] O. Toulemonde, F. Studer, A. Barnabé, A. Maignan, C. Martin, and B. Raveau, Eur. Phys. J. B **4**, 159 (1998).

[6] J. van Elp, Phys. Rev. B **60**, 7649 (1999).

[7] Z. Tan, S. M. Heald, S.-W. Cheong, A. S. Cooper, and A. R. Moodenbaugh, Phys. Rev. B **47**, 12365 (1993).

[8] M. Croft, D. Sills, M. Greenblatt, C. Lee, S.-W. Cheong, K. V. Ramanujachary, and D. Tran, Phys. Rev. B **55**, 8726 (1997).

[9] G. Subías, J. García, M. G. Proietti, and J. Blasco, Phys. Rev. B **56**, 8183 (1997).

[10] Z. Hu, M. S. Golden, J. Fink, G. Kaindl, S. A. Warda, D. Reinen, Priya Mahadevan, and D. D. Sarma, Phys. Rev. B **61**, 3739 (2000).

[11] O. Toulemonde, F. Studer, and B. Raveau, Solid State Commun. **118**, 107 (2001).

[12] C. Mitra, Z. Hu, P. Raychaudhuri, S. Wirth, S. I. Csiszar, H. H. Hsieh, H.-J. Lin, C. T. Chen, and L. H. Tjeng, Phys. Rev. B **67**, 092404 (2003).

[13] T. Kyômen, R. Yamazaki, and M. Itoh, Phys. Rev. B **68**, 104416 (2003).

[14] A. Yu. Ignatov, N. Ali, and S. Khalid, Phys. Rev. B **64**, 014413 (2001).

[15] L. Hozoi, A. H. de Vries, and R. Broer, Phys. Rev. B **64**, 165104 (2001).

[16] Y. Joly, D. Cabaret, H. Renevier, and C. R. Natoli, Phys. Rev. Lett. **82**, 2398 (1999).

[17] Z. Y. Wu, D. C. Xian, T. D. Hu, Y. N. Xie, Y. Tao, C. R. Natoli, E. Paris, and A. Marcelli, Phys. Rev. B **70**, 033104 (2004).

[18] F. Bridges, C. H. Booth, M. Anderson, G. H. Kwei, J. J. Neumeier, J. Snyder, J. Mitchell, J. S. Gardner, and E. Brosha, Phys. Rev. B **63**, 214405 (2001).

[19] C. Autret, J. Hejtmánek, K. Knížek, M. Maryško, Z. Jirák, M. Dlouhá, and S. Vratislav, J. Phys.: Condens. Matter **17**, 1601 (2005).

[20] O. Hass, R. P. W. J. Struis, and J. M. McBreen, J. Solid State Chem. **177**, 1000 (2004).

[21] Edge positions were calculated analytically as the maximum of the first derivative of the third-order polynomial, obtained from interpolation of the measured spectra in the range of 4–7 eV (equivalent to 9–15 experimental points).

[22] M. C. Sánchez, J. García, J. Blasco, G. Subías, and J. Pérez-Cacho, Phys. Rev. B **65**, 144409 (2002).

[23] M. C. Sánchez, G. Subías, J. García, and J. Blasco, Phys. Rev. B **69**, 184415 (2004).

[24] A. H. de Vries, L. Hozoi, and R. Broer, Int. J. Quantum Chem. **91**, 57 (2003).

[25] V. Procházka *et al.* (in preparation).