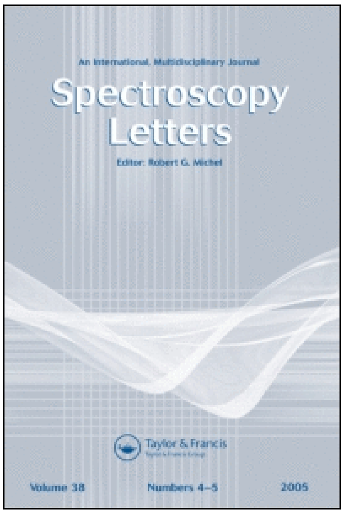

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Evaluation of the Mn Lα and Lβ Spectra of Mn Metal and of Various Mn-Oxides

N. Yoshikawa[a]; G. Andermann[a]; F. Fujiwara[a]; T. Scimeca[a]
[a] Department of Chemistry, University of Hawaii at Manoa Honolulu, Hawaii

To cite this Article Yoshikawa, N. , Andermann, G. , Fujiwara, F. and Scimeca, T.(1997) 'Evaluation of the Mn Lα and Lβ Spectra of Mn Metal and of Various Mn-Oxides', Spectroscopy Letters, 30: 7, 1211 — 1225
To link to this Article: DOI: 10.1080/00387019708006719
URL: http://dx.doi.org/10.1080/00387019708006719

SPECTROSCOPY LETTERS, 30(7), 1211-1225 (1997)

EVALUATION OF THE Mn Lα AND Lβ SPECTRA OF Mn METAL AND OF VARIOUS Mn-OXIDES

Key Words: X-ray emission spectroscopy; L emission; Mn-oxides; crossover transitions

N. Yoshikawa, G. Andermann[+], F. Fujiwara, and T. Scimeca.

Department of Chemistry
University of Hawaii at Manoa
Honolulu, Hawaii 96822

ABSTRACT

The Mn Lα and Lβ spectra of Mn, MnO, Mn_3O_4, Mn_2O_3, and MnO_2 have been measured. Each Mn Lα spectrum has been deconvoluted into two bands, $L\alpha_A$ and $L\alpha_B$, and the integrated $L\alpha_A/L\alpha_B$ intensity ratio was found to be inversely proportional to the Mn-O inter-atomic distance, but proportional to the oxidation number. This finding tends to indicate the likelihood of crossover transition from oxygen to manganese. The intensity ratio $L\beta/L\alpha_B$ of the pure metal was found to coincide closely with the statistically predicted value of 0.5.

[+] To whom any correspondence should be addressed

Furthermore, for Mn-metal, as well as for the oxides, the shift of the $L\alpha_A$ band from the $L\alpha_B$ band was found to agree with the change in the $L\beta/L\alpha$ peak intensity ratio as a function of oxidation number.

INTRODUCTION

The dependence of the intensities, shapes, and wavelengths of the $L\alpha_{1,2},\beta$ diagram transitions of Mn metal have been studied by a number of people(1,2,3). The $L\alpha_{1,2}$ and $L\beta$ bands correspond to the $3d_{3/2,5/2}$--$2p_{3/2}$ and $3d_{3/2}$--$2p_{1/2}$ transitions, respectively. The effects of oxidation on electron excited L emission bands of the elements from Z=20 to Z=30 was first evaluated in detail by Fischer(1). Galakhov, et al.(2) also investigated the $L\alpha,\beta$ emission spectra of Mn and Mn-oxides using electron excitation. Since the effective number of unpaired 3d electrons increases in the series Mn, MnO_2, Mn_2O_3, MnO, he suggested that the one-center 2p-3d exchange interaction may influence the variation in the observed relative intensities of the $L\beta$ and $L\alpha$ spectra.

For pure Mn metal, the conventional reason given by some workers for the experimentally observed $L\beta/L\alpha$ intensity ratio being considerably lower than the statistically expected (1:2) has been ascribed to the radiationless process $L_2L_3M_{4,5}$(2,5). Accordingly, at the expense of the L_2 holes, the Coster-Kronig Auger process leaves vacancies in the L_3 and $M_{4,5}$ states(6). Therefore, it was believed that the Coster-Kronig Auger process promotes the $L\alpha$ transition and represses the $L\beta$ transition. However, the Coster-Kronig Auger process yields a doubly ionized final state, hence, subsequent radiative transitions from the 3d level would be expected to emit hyper-satellites(6,7) on the high photon energy side of the main $L\alpha$ peak. In other words, for the doubly ionized state the transition emits a different photon energy than when it is in a singly ionized state. Hence, if the Coster-Kronig Auger process does take place, it reduces the yield of both the Lβ and Lα emissions, and its effect on the Lβ/Lα intensity ratio should be insignificant.

For manganese oxides, different kinds of arguments were held for variation in the observed Lα/Lβ ratio. Hallmeier, et al.(3) used a primary X-ray beam from a copper anode and correlated the deconvoluted Mn Lα and O Kα bands of MnO_2. They claimed that their observation indicated a chemical bonding interaction of O-2p and Mn-3d states. Recently, Galakhov, et al.(4) reported that the Mn-3d, O-2p mixing in MnO gives rise to a short-wavelength shoulder in the O Kα spectrum which coincides with the Mn Lα maximum. The assumption by Hallmeier and Galakhov was that the ligand oxygen 2p orbitals mixes with the manganese 3d electron orbitals.

Another possibility for the unusual Lα/Lβ behavior is crossover transition from oxygen to manganese. This had been rejected by Urch(8), who argued against such transitions. More recently, however, Rowlands and Larkins(9) have argued on behalf of crossover transitions. Our objective in this research is to evaluate the possibility of such transitions. In view of the possibility that the low-energy band structure of the Lα emission band may be due to crossover transitions, we undertook the careful deconvolution of the Lα bands.

EXPERIMENTAL STUDIES

Curve Deconvolution

Limitations of instrumental resolution prevents overlapping spectral bands from being resolved into discrete bands. Spectral deconvolution is a useful technique to extract the pertinent information in studying the Lβ and Lα spectra. Therefore, the Mn Lα emission spectra of Mn metal and its oxides were deconvoluted via a Self-Bracketing Search(10), SBS, computer program. Since all of the Lα bands show asymmetry on the low photon energy side, our objective in our deconvolution scheme was to see whether or not we could break up the Lα band into two components. For Mn-oxides, asymmetry seems to exist also for the Lβ bands. Although the Lβ bands were not deconvoluted, because of the weakness of the SBS program, the lower energy sides of the Lβ band in all oxide spectra appear to have a shoulder. The Lβ band asymmetry requires further investigation.

The SBS computer program was tested on synthetically generated spectra for its reliability. The results show that this program has an inherent weakness in that it allocates more intensity to a lower-intensity peak by reducing the intensity of the adjacent higher-intensity peak. This effect is troublesome only when the lower-intensity peak is less than 10 % of the adjacent higher-intensity peak, and/or when these peaks are situated too close (about 1-2 eV) to each other. Since these troublesome features do not exist in the Lα spectra of Mn-oxides, the SBS program has served as a reasonable tool for studying the Mn Lα spectra quantitatively.

Spectroscopic Measurements

The spectra of Lα and Lβ for Mn metal and Mn-oxides were obtained on our 5 M grating ultrasoft X-ray fluorescence spectrometer(11) using photon excitation via a Henke X-ray tube(12) operated at 8 kV and I=160-180 mA. All spectra were in the first order with the instrumental resolution of 2.8 eV.

The spectra were detected with a photoelectric scanner using a gas proportional counter. The vacuum in the spectrometer chamber was less than 1.0×10^{-5} torr. The investigated samples were highly pure Mn metal, MnO, Mn_3O_4, Mn_2O_3, and MnO_2. The oxide samples were bought commercially and studied directly without further purification.

RESULTS AND DISCUSSION

Fig. 1 shows our Mn Lα and Lβ X-ray emission spectra and these are very similar to those previously reported by Galakhov(2). Their spectroscopic resolution appears to be similar to ours. The Lα transitions of Mn metal has the narrowest band and is slightly asymmetric, with a slight shoulder at the lower photon energy side of the Lα band. All of the manganese oxides Lα spectra show greater asymmetry than Mn-metal. Mn Lα bands have been deconvoluted and arbitrarily noted as $L\alpha_A$ and $L\alpha_B$, with A representing the lower photon energy band. These bands do not correspond to the $L\alpha_1$ and $L\alpha_2$ bands, respectively, because their peak separation is too large in comparison to the theoretical resolution of the $L\alpha_{1,2}$, which is much less than 1.0 eV. On the other hand, it is reasonable to assume that the $L\alpha_B$ band represents the true $L\alpha_{1,2}$ transitions, since the $L\alpha_B$ peak position closely coincides with that of the undeconvoluted experimentally obtained Lα band. Areas under the Lβ bands were obtained by using the SBS method assuming a single transition.

Our results of the peak (i.e. before deconvolution) Lβ/Lα intensity ratios are listed on Tab. 1. Our findings show similar trends to those by Galakhov(2), that is, the ratios (see Fig. 2) increase sharply on passing from the pure metal to MnO, and then decrease gradually on passing to higher oxidation

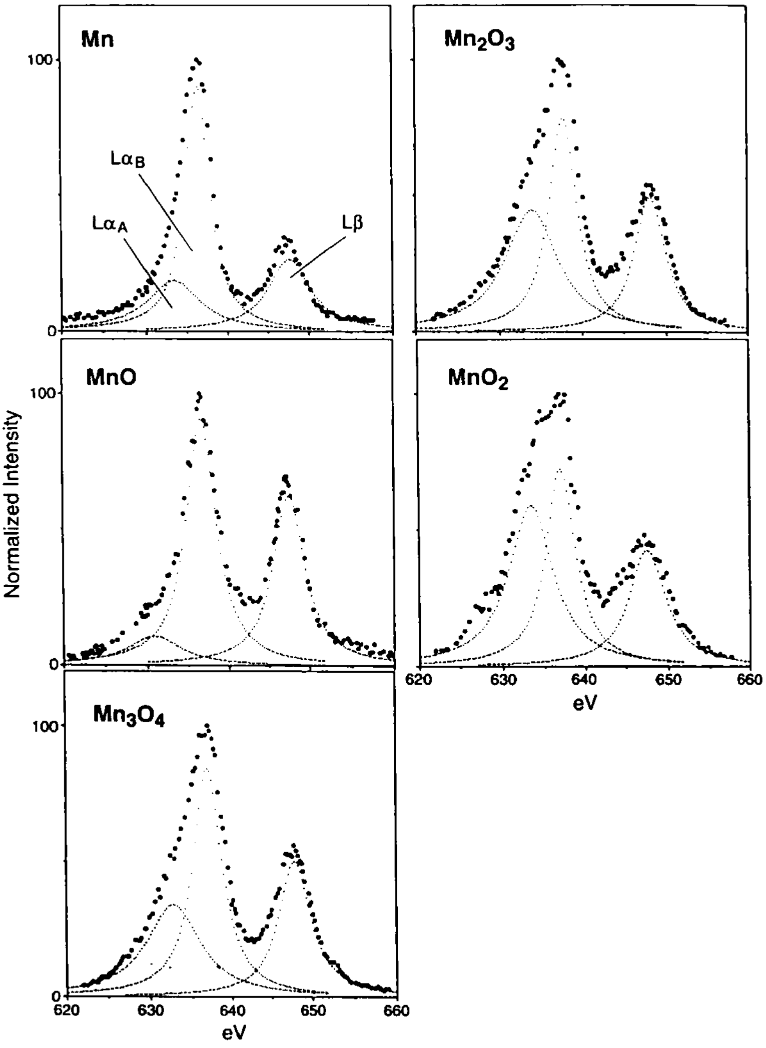

FIG. 1. X-ray La,β Emission Spectra of Mn-Metal and Its Oxides.

TABLE 1

Relative Mn L Emission Intensity Ratios of Literature and Experimental Values.

Compound	a) Lβ/Lα (peak)	b) Lβ/Lα (Integrated)	c) Lβ/Lα (peak)
Mn	0.19	0.19	0.36
MnO	0.89	0.90	0.73
Mn_3O_4	0.76	0.76	0.56
Mn_2O_3	0.66	0.68	0.53
MnO_2	0.53	0.53	0.48

The header "Intensity Ratios" spans columns a), b) and c).

a) & b): Values Obtained from Ref. (2) (electron excitation).
c) Experimental values (photon excitation).

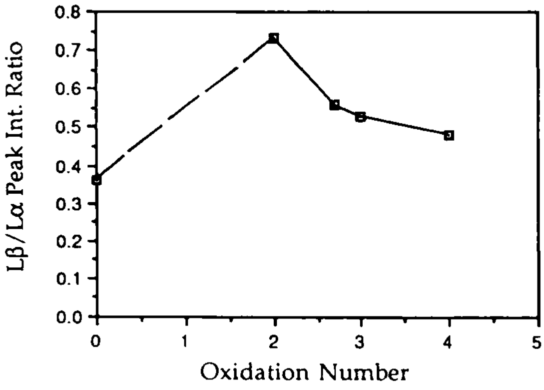

FIG. 2. Dependence of Lβ/Lα Relative Peak Intensity Ratio on the Oxidation Number for Mn and Mn-oxides.

states. Despite the similarity in the trend, except for Mn metal the ratios appear to be generally higher in reference 2 than obtained by us. This discrepancy is attributed to differences in excitation sources.

In Tab. 2 we provide the experimentally observed $L\alpha_A/L\alpha_B$ integrated intensity ratio values for Mn metal as well as for all its oxides. We estimate that the intensity ratios are reliable to about 3 to 5%. This table also lists a number of parameters which turn out to be highly significant in interpreting the experimental findings, namely, the ratio of oxygen atoms to the Mn atoms for each species, as well as the Mn-O interatomic distance r, as well as the reciprocal of r.

In the case of Mn-oxides, as discussed below, our observations tend to support the two-center or crossover transition model, according to which the $L\alpha_A$ band is due to this crossover transition. Our viewpoint is based specifically on the model of Rowlands and Larkins(9), whose calculation of X-ray transition probabilities for a carbon monoxide molecule revealed increasing contribution of crossover transition as the bond length between the carbon and oxygen decreases. Manganese is a much larger atom than carbon; however, we observed similar trends in intensity as a function of Mn and oxygen inter-atomic distance, thus indicating that for the $L\alpha_A$ band, the crossover transition is probably a useful model. In other words, as the bond length between manganese and oxygen decreases, the $L\alpha_A/L\alpha_B$ intensity ratio increases. It is important to mention, however, that, as expected, the decrease in the inter-atomic distance between manganese and oxygen is caused by an increasing number of oxygen ligands per manganese atom, as indicated in Fig. 3. As the number of oxygen ligands increases on manganese, the electron

TABLE 2

Ratio of Number of Oxygen to Mn Atoms, $L\alpha_A/L\alpha_B$ Relative Integrated Intensity, Average Inter-atomic Distances Between Manganese and Oxygen, and Reciprocal of Inter-atomic Distance Between Mn and O.

	Intensity Ratio			
Compound	a) $L\alpha_A/L\alpha_B$ (integrated)	b) N_O/N_{Mn}	c) $r_{Mn\text{-}O}$	d) l/r
Mn	0.45	---	---	
MnO	0.21	1.00	2.22(14)	0.450
Mn_3O_4	0.74	1.33	2.05(15)	0.488
Mn_2O_3	1.06	1.50	2.01(15)	0.498
MnO_2	1.22	2.00	1.90(16)	0.526

a) Experimental values (photon excitation).

b) N_O/N_{Mn} = Ratio of number of oxygen to Mn atoms.

c) $r_{Mn\text{-}O}$ = ave. inter-atomic dist. between Mn and O (Å). See references (14 through 16).

d) l/r = reciprocal of inter-atomic distance between Mn and O.

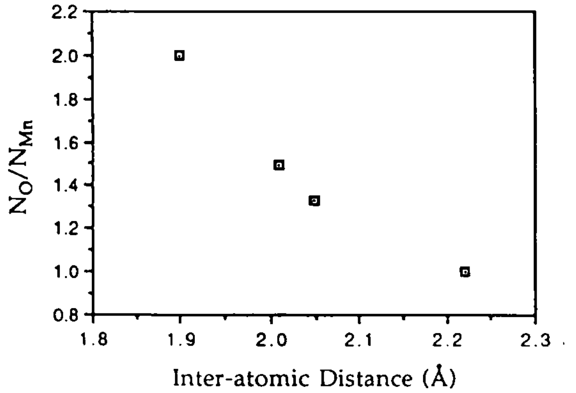

FIG. 3. Ratio of Number of Oxygen to Mn Atoms vs. Inter-atomic Distance Between Oxygen and Mn.

density on the manganese decreases, but enhanced oxygen and manganese orbital overlap forming a bond, forces oxygen and manganese atoms to be closer. Therefore, the likelihood of crossover transition should increase with the increasing number of oxygen ligands on manganese. This phenomenon is shown in Fig. 4. It should be noted that both in Figures 3 and 4 MnO and MnO_2 plot most differently, yet Mn in both substances is octahedrally coordinated.

Fig. 5 shows a linear relationship between the intensity ratio of the $L\alpha_A/L\alpha_B$ and the inter-atomic distance between Mn and oxygen. Accordingly, for a 17% decrease in inter-atomic distance, the intensity ratio has increased by a factor of 6.

Startling similarity between Figs. 2 and 6 shows that for Mn-metal, as well as for the oxides, the dependence of the energy peak separation between the $L\alpha_A$ band and $L\alpha_B$ band upon the oxidation number is similar to that of the $L\beta/L\alpha$ intensity ratio. Numerical data are listed in Tab. 3. This table also provides the integrated $L\beta/L\alpha_B$ values. As stated already we consider $L\alpha_B$ to be the true $L\alpha_{1,2}$ band.

As shown in Tab. 3, the $L\alpha_A$ peak position decreases in energy significantly in going from Mn metal to MnO, and then gradually increases on passing to higher oxides. These shifts suggest that the origin of their transitions may be different, and that these discrepancies will need to be explained in terms of either one-center and two-center models. Koster(13) explained the origin of the $L\alpha_A$ peak in Mn metal in terms of a one-center model. He suggested that a transition from Mn 4s electrons is causing the appearance of the $L\alpha_A$ band at the lower photon energy side of $L\alpha$. If this

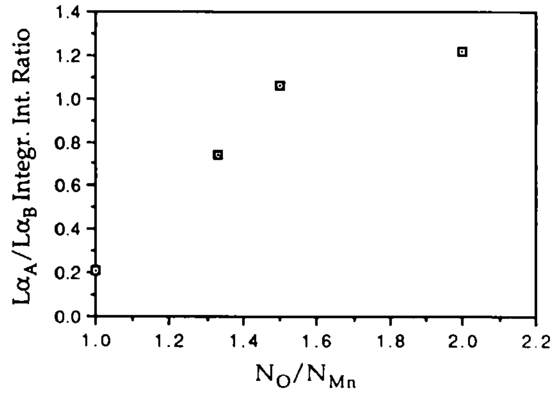

FIG. 4. The $L\alpha_A/L\alpha_B$ Integrated Intensity Ratio vs. Ratio of Number of Oxygen to Mn Atoms.

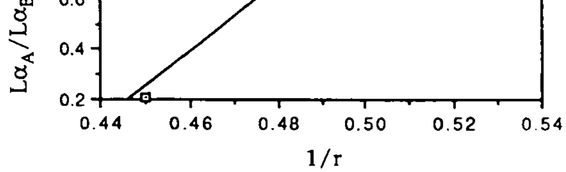

FIG. 5. $L\alpha_A/L\alpha_B$ Integrated Ratio vs. Reciprocal of Inter-atomic Distance Between Mn and O.

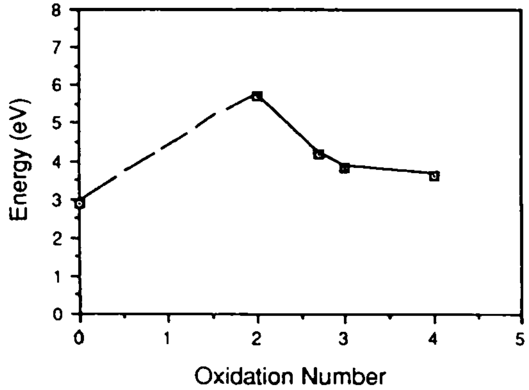

FIG. 6. Dependence of Energy Peak Separation Between $L\alpha_A$ and $L\alpha_B$ on Oxidation Number.

TABLE 3

Effect of Oxidation Number on Peak Positions.

Compound	Peak Position			Intensity
	a) Ox. No.	b) $L\alpha_A$ (eV)	c) $L\alpha_B$ (eV)	d) $L\beta/L\alpha_B$ integrated
Mn	0.0	633.4	636.3	0.53
MnO	+2.0	630.9	636.6	0.77
Mn_3O_4	+2.7	632.8	637.0	0.68
Mn_2O_3	+3.0	633.8	637.6	0.69
MnO_2	+4.0	633.4	637.0	0.73

a) Ox. no. = Oxidation Number

b) c): Experimental values (photon excitation).

d) $L\beta_B = L\alpha_{1,2}$

assumption by Koster is correct, then the SBS program has enabled us to subtract the 4s contributions from the Lα band of the metal, and has revealed the true $L\alpha_{1,2}$ band as being the $L\alpha_B$ band. It is noteworthy that the integrated intensity ratio of the Lβ to the true $L\alpha_{1,2}$ band results in a value of 0.53, which is approximately equal to the statistically predicted value of 0.50. This deconvoluted result supports a reinterpretation of the rationale suggested by Wood and Urch(6), namely, that the Coster-Kronig Auger effect does not affect the $L\beta/L\alpha_{1,2}$ ratio. Therefore, at least for the Mn-metal, one could argue that the $L\beta/L\alpha_{1,2}$ intensity value would significantly change if the Lβ band were to be resolved into two discrete bands. However, the Lβ band appears very symmetric for Mn metal, therefore, contribution from a concealed satellite band, if there is any, must be insignificant in the Lβ band as a whole.

CONCLUSION

The increase in the intensity of $L\alpha_A$ peak with respect to the $L\alpha_B$ peak is attributed to the rise in the intensity of the undeconvoluted Lα peak, and, hence, it is clear now that the mystery of the Lβ/Lα ratio dependency on oxidation of manganese should be attributed to the appearance of the $L\alpha_A$ peak. Our observation suggests the possibility that the $L\alpha_A$ peak is due to the two center model's crossover transition from oxygen to manganese. The $L\alpha_A/L\alpha_B$ peak intensity ratios reflect the proportionality of the oxygen - manganese ratio, and also the interatomic distance between manganese and oxygen. Hence, a satellite structure at the lower photon energy side of the Lα band reveals the nature and type of chemical bond between metal and its ligand. Additionally, it is shown for the first time, by means of spectral deconvolution, that the Croster-Kronig Auger process does not effect either rise or fall of the Lβ/Lα peak intensity ratio for pure manganese, but that the transition from the 4s level is the likely cause for the Lβ/Lα peak intensity ratio being lower than the statistically predicted ratio. Furthermore, for Mn-metal, as well as for the oxides, the shift of the $L\alpha_A$ band from $L\alpha_B$ band was found to agree with the change of the Lβ/Lα intensity ratio. Investigating oxygen K and L lines dependency on manganese oxidation number should reveal further evidence of the validity of using the two-center model.

REFERENCES

1. Fischer, D.W., J. Appl. Phys. 1965; 36:6,2048-53.
2. Galakhov, V.R., Kurmaev, E.Z., and Cherkashenko, V.M. Izv. Akad. Nauk SSSR, Ser.Fiz. 1985; 49:8,1513-1517.
3. Hallmeier, K.H., Szargan, R., Fathrin, K., and Meisel A. Physica Scripta 1987; 35:827-830.
4. Galakhov, V.R., Butorin, S.M., Kurmaev, E.Z., and Kovotin, M.A. Physica B 1991; 68:163-169.
5. Skinner, H.W.B., Bullen, T.G., and Johnston, J.E., Phil.Mag. 1954; 45:1979.
6. Wood, P.R., and Urch, D.S. J. Phys.F: Metal Phys. 1978; 8:3,543-553.
7. Wood, P.R., and Urch, D.S. J.Chem. Soc.(Dalton Trans.) 1976; 2472-2476.
8. Urch, D.S., J.Phys. 1970; C3:1275.
9. Rowlands, T.W., and Larkins, F.P., Theor.Chim.Acta 1986; 69:525-534.
10. Ronald A. Lynch, Master's thesis, Univ. of Hawaii at Manoa; 1974.

11. Andermann, G. Appl.Surface Science 1988; 31:1-41.

12. Henke, B.L. and Tester, M.A., Advances in X-ray Analysis, vol.18, Plenum Press; 1975.

13. Koster, A.S., Proc.Kon. Ned. Akad. Wet B. (Netherlands) 1971; 74:3,332-9.

14. Broch, E., Z.Physik.Chem. 1927; 127:446-54.

15. Norrestan, R., Acta Chem. Scand. 1967; 21:10,2871-2884.

16. Rogers,D.B., Shannon,R.D., Sleight, A.W., and Gillson, J.L., Inorganic Chem. 1969; 8:4.

Date Received:September 23, 1996
Date Accepted:May 23, 1997