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M. Belli, A. Bianconi, E. Burattini, S. Mobilio, L. Palladino,
A. Reale and A. Scafati: X-RAY ABSORPTION NEAR EDGE
STRUCTURES (XANES) IN SIMPLE AND COMPLEX Mn
COMPOUNDS.

X-RAY ABSORPTION NEAR EDGE STRUCTURES (XANES) IN SIMPLE
AND COMPLEX Mn COMPOUNDS^(x)

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ABSTRACT: The X-ray Absorption Near Edge Structures (XANES) of Mn compounds at the Mn K-edge have been measured with high resolution at the Frascati Synchrotron Radiation Facility "PULS". Molecular effects, such as "shape resonances", have been identified in molecular complexes. Experimental evidence of solid state (or long-range order) effects have been found in spectra of simple oxides.

The application of XANES for determining the local structure and chemical bonding of Mn ion in unknown compounds is discussed.

(x) - Part of this work was performed at the Project for the Utilization of Synchrotron Light "PULS" which is supported by CNR-GNSM and INFN.

1. - INTRODUCTION.

X-ray absorption spectroscopy using synchrotron radiation sources, is rapidly growing and it is now an important tool for investigating the local structures of materials and molecules by the analysis of the EXAFS structures⁽¹⁾. The use of the analysis of the X-ray Absorption Near Edge Structures (XANES), extending up to ~ 40 eV above the K threshold⁽²⁾, to obtain structural information, is growing more slowly. There is not a simple theoretical formula, like for EXAFS⁽³⁻⁸⁾, to fit the XANES and some fundamental aspects of the physics of the near edge structures have been clarified only recently⁽⁹⁾. If the XANES are determined by molecular effects, the dependence of the oscillator strength and of the energy shift of the individual absorption peaks on the local symmetry and on the chemical bonding, can be determined by measuring the K edge spectra of several model compounds with known microscopic structure. After such a study, structural information of unknown local structures can be extracted from near edge spectroscopy. This approach requires high resolution spectra, which are now possible to obtain by using synchrotron radiation.

In some cases the simple molecular approach is not adequate to explain XANES. For example in the case of metals and rare gas solids the effect of long range order on the final state wave functions cannot be disregarded. In the case of transition metal oxides such effects can be important due to the direct metal-metal interactions. In fact we have found that solid state effects have to be taken into account in simple Mn oxides.

In this work we have studied the XANES of Mn compounds to understand the physical origin and the effect of the chemical bonding on these structures. The interest is focused on Mn ions octahedrally coordinated to oxygens, in view of extending this investigation on more complex biological molecules such as ribonucleic acids and ribonucleoproteins.

We have measured the XANES of Mn compounds with higher resolution and signal-to-noise ratio than previous measurements⁽¹⁰⁾ made with standard sources. We have found that the molecular approach can explain the XANES of Mn complexes while solid state effects appear in the spectra of simple oxides.

2. - NEAR EDGE STRUCTURES IN MOLECULAR COMPLEXES.

The XANES of molecules MX_n formed by the photoabsorbing central atom M and its ligands X_n have been theoretically interpreted⁽¹¹⁾. The final states of core transitions are both empty valence states and shape resonances extending both in the discrete and continuum part of the spectra. Also the final states in the continuum are localized inside the molecule. This occurs when the amplitude probability $A(K)$ (where \vec{K} is the photoelectron wavevector) of the photoelectron backscattering from the X_n atoms is large at low \vec{K} values. In this situation the final state wavefunction at the resonance energies is confined inside the MX_n molecule by an effective potential which is due to the combined effect of the centrifugal potential acting on the high l components of the final state wavefunction⁽⁹⁾ and of the Pauli exclusion principle which expels the photoelectron from the region of high valence electron density localized on the electronegative X_n atoms⁽¹¹⁾.

In condensed matter we can extend the same interpretation of the XANES if these structures are determined only by the microscopic MX_n cluster formed by the metal and its first neighbours X_n . We expect that this occurs when there is no long range order or it is poor, like for ions in solution or complexes. If the XANES are dominated by "shape resonances" or "inner well states" an empirical approach can be used to determine unknown local structures, by comparing XANES spectra of a number of model compounds of known local structure with the spectra of unknown samples. In fact if the spectrum of the sample and that of one of the model compounds are similar the local structure will be similar. This approach has been

used also to determine the site structure of a metal atom in biological molecules^(2, 12).

3. - EXPERIMENTAL.

The experiments were made at the Synchrotron Radiation Facility PULS at the Frascati Laboratories. Synchrotron Radiation emitted by the Adone storage ring, working at 1.5 GeV and about 50 mA, was monochromatized by a Si(220) channel cut single crystal monochromator. The energy resolution at 7 keV is $\Delta E/E \approx 10^{-4}$. The stated energy differences between two absorption peaks in the derivative of absolute spectra are accurate to ± 0.1 eV. The high intensity and the stability of the monochromatic X-ray beam allow exceptional high signal to noise ratio and high resolution X-ray absorption spectroscopy in comparison with spectra taken with standard X-ray tubes. The absorption coefficient has been calculated from transmission data T using the formula $\alpha = -(1/d) \ln T$ where d is the thickness of the sample. Samples were films, few microns thick, of powder layered on a Kapton tape. Many of them were high purity products obtained from Merck and Alpha; MnATP complexes were prepared by adding equimolar quantities of $MnCl_2$ to concentrated aqueous solutions of 5'-Adenosin Monophosphate and 5'-Adenosin Triphosphate respectively, supplied by Boehringer Biochemia; these preparations were then freeze-dried. The sample thickness was chosen in order to obtain the better contrast at the K edge. Several samples of each compound of thickness such that $\alpha d \sim 1$ have been used, ranging from 5 to 20 mg/cm²; the higher values were for organic samples due to their relatively lower Mn concentration. Data acquisition and elaboration were done by using a PDP 11 computer. The zero energy of the photon energy scale has been taken at the first maximum of the derivative spectrum of metal Mn.

4. - RESULTS.

Fig. 1 shows the X-ray absorption spectra of the Mn compounds. Fig. 2 shows the first derivative of the X-ray absorption spectra of the Mn oxides. In all these compounds the Mn ions are coordinated with 6 oxygen ions, except for KMnO_4 where Mn has a tetrahedral coordination. The structure called A is very weak in the compound where the coordination number is 6, on the contrary it is very strong where the coordination number is 4. In the derivative spectra in Fig. 2 it is possible to identify several weak structures which are very difficult to see in the absorption spectra in Fig.1. In Fig. 3 the absorption derivative of a series of Mn phosphate compounds are plotted. In all these compounds the formal state of charge of the Mn ions

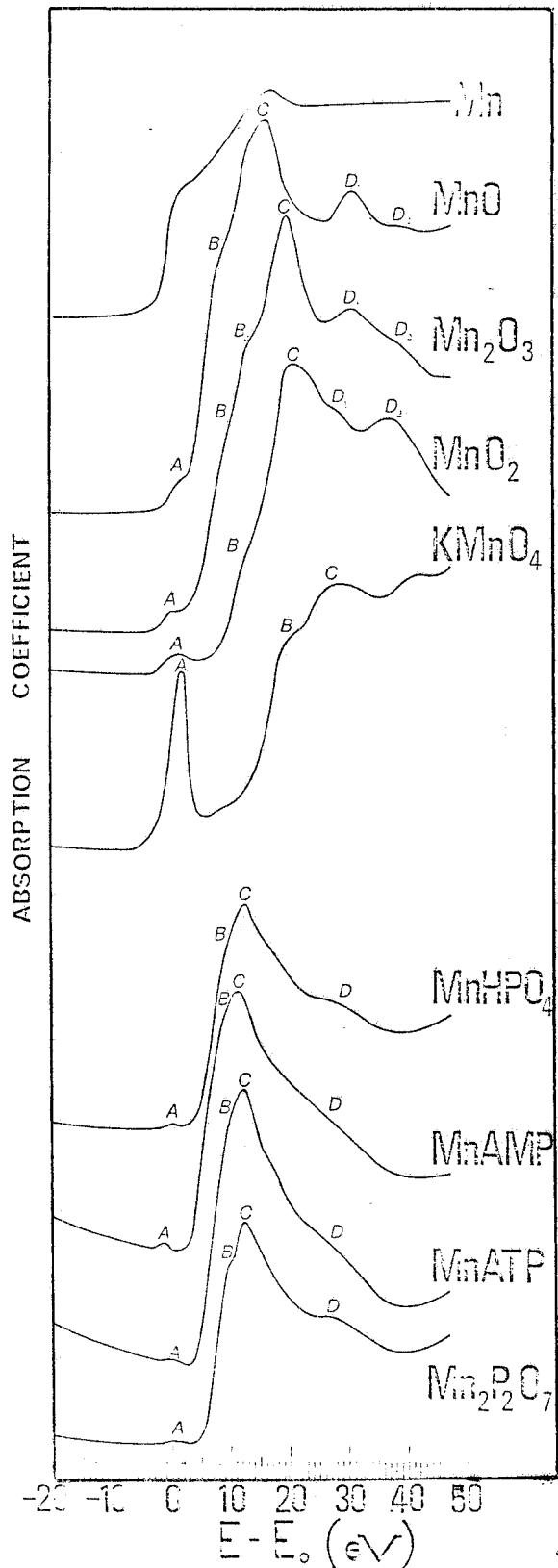


FIG. 1 - X-ray absorption coefficient vs. photon energy difference, $E - E_0$, where $E = \hbar\omega$, and E_0 is the zero of the photon energy scale, taken at the first maximum of the derivative spectrum of the metal Mn.

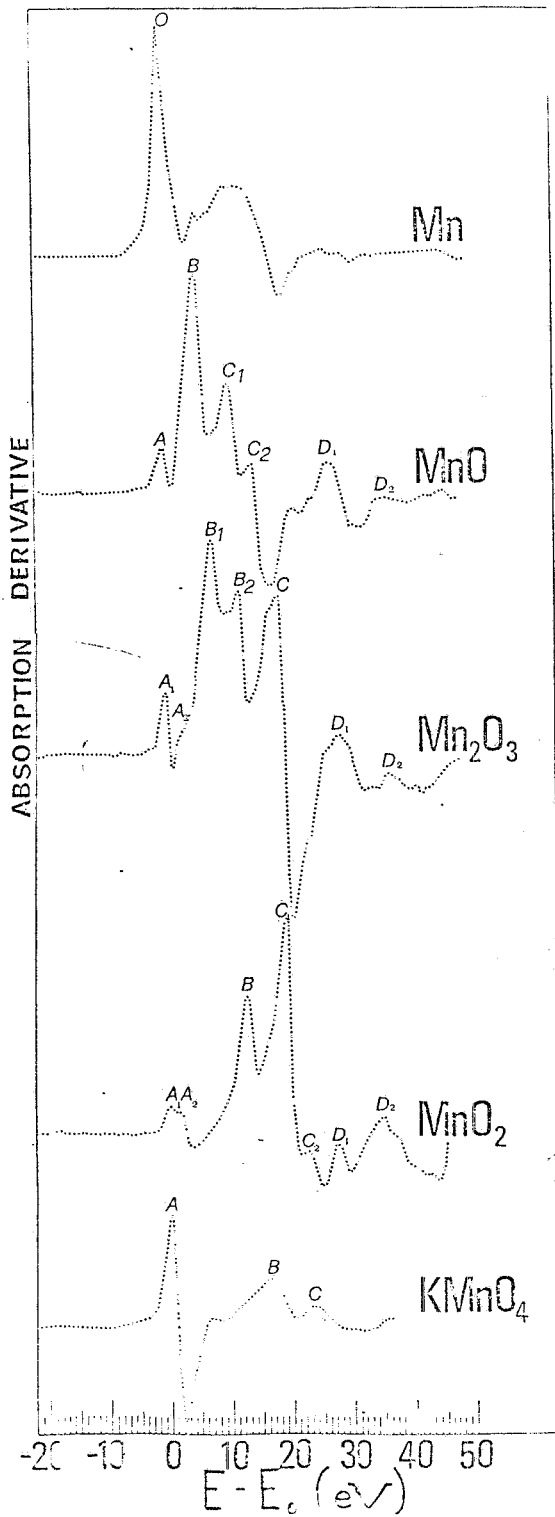


FIG. 2 - First derivative of X-ray absorption coefficient of Mn oxides and KMnO₄.

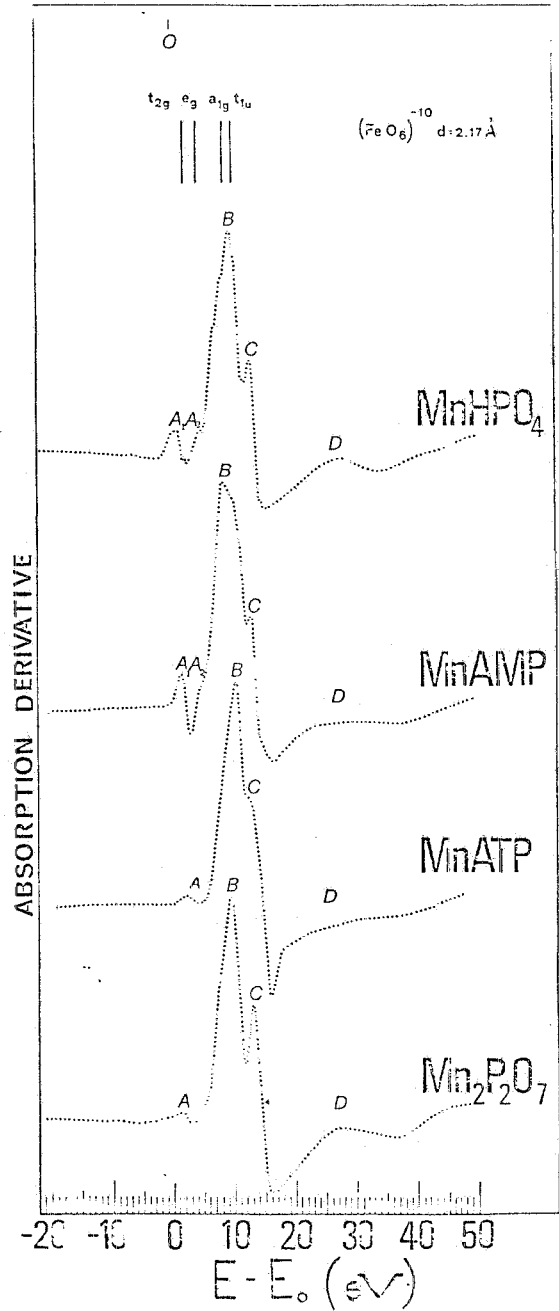


FIG. 3 - First derivative of X-ray absorption coefficient of Mn phosphate compounds. The molecular excited states of $(\text{FeO}_6)^{-10}$, which in the $(Z+1)$ analogy should correspond to same final excited states of Mn at K-edge are also reported.

is 2. The coordination number (CN) of the $Mn_2P_2O_7$ compounds is 6, but it is not well established for the Mn-Adenosine-Monophosphate and Mn-Adenosine-Triphosphate. In these last compounds of biological interest Mn is expected to be coordinated with PO_4 . These spectra are simpler than the spectra of oxides in Fig. 2. The peak A in MnATP spectrum is weaker in comparison with the MnAMP spectrum.

5. - DISCUSSION.

5.1. - Molecular effects.

We have selected samples where Mn is always coordinated by six oxygen ions in order to study the effect of structural environment on the XANES. To establish the effect of long range order on the XANES we have chosen a series of complex compounds in Fig. 3 where the degree of structural order out of the first coordination shell is lower in comparison with the spectra of simple oxides in Fig. 2. By comparing the spectra in Fig. 2 and Fig. 3 it is clear that the spectra of simple oxides exhibit more fine structures. These were not all observed in previous measurements of simple oxides^(10, 13-18) with showed only the main, A, B, C peaks, since they were made with lower resolution and signal-to-noise ratio. In order to obtain experimental evidence of molecular effects alone we have measured the XANES of Mn^{2+} ion in water solution. The spectrum shown in Fig. 4 is determined only by the MnO_x cluster and it is similar to the spectra in Fig. 3. It exhibits only the main B, C, D structures. Also from a theoretical point of view if the XANES are determined only by the MnO_6 microscopic cluster (i. e. by molecular effects) only the structures A, B, C, D are expected. The first excited states of the molecular MnO_6 cluster can be derived by using the molecular $(Z+1)$ analogy⁽²⁾. In this case the excited states calculated for the FeO_6 cluster should correspond to the same final excited states at the K edge of MnO_6 . The molecular excited states of $(FeO_6)^{-10}$ have been calculated by Tossel et al.⁽¹⁹⁾ and are reported in Fig. 3. The average Mn-O distance in

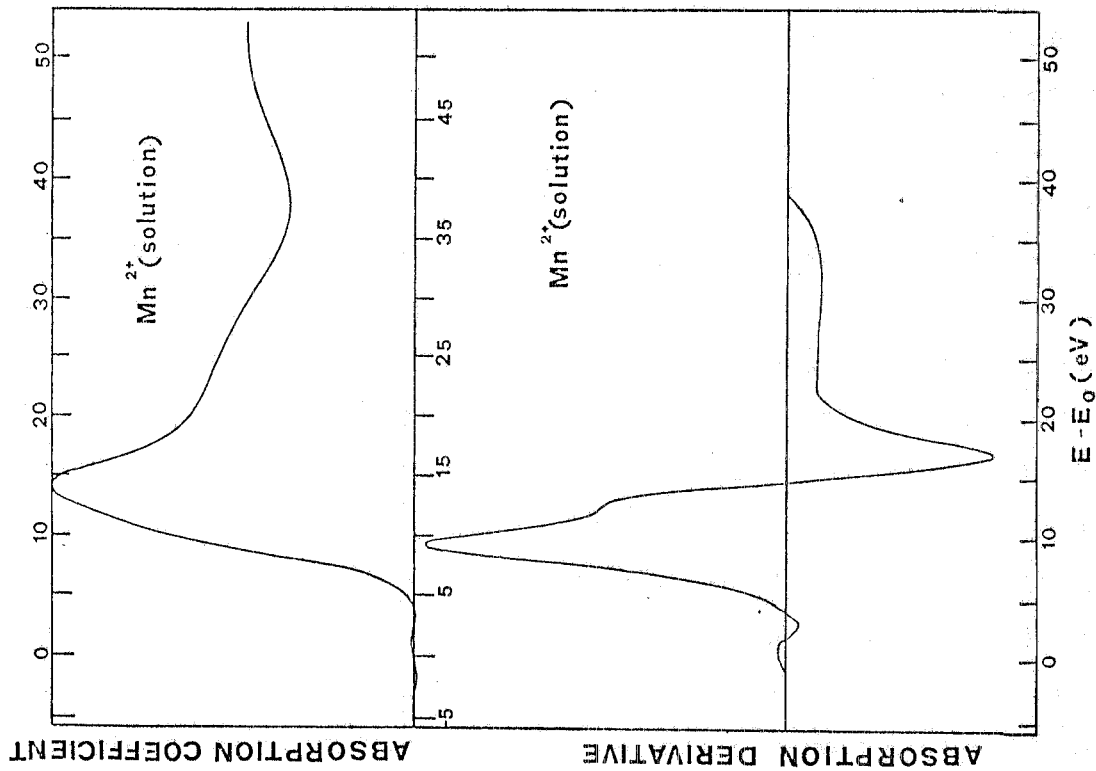


FIG. 4 - X-ray absorption coefficient and first derivative of MnCl_2 solution.

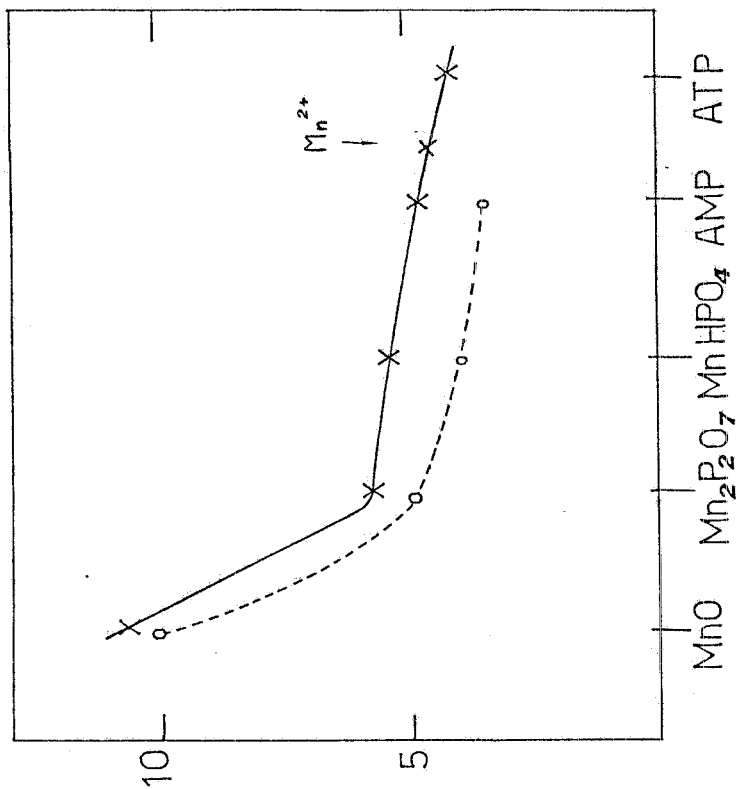


FIG. 5 - Splitting of the shoulder B and peak C in different compounds with the same Mn valency and coordination number (crosses, xxx). The points (ooo) are the values of the energy separation between the peaks B and C in derivative spectra.

Mn compounds (about 2.2 \AA) is similar to the Fe-O distance in $(\text{FeO}_6)^{-10}$. Also the valency of the Mn ion is like that of Fe in the $(\text{FeO}_6)^{-10}$ cluster. A good agreement is found for the energy separation between the structures A₁, A₂, B and the calculated empty antibonding valence states t_{2g} , e_g , t_{1u} respectively.

The shoulder B can be assigned⁽²¹⁾ to the continuum threshold of core transitions to dipole allowed p-like states of t_{1u} symmetry. The peak C should be due to a "shape resonance" in the continuum part of the spectrum^(9, 11). In Fig. 5 we report the energy separation of these features, which is clearly dependent on the Mn-O bonding in different compounds. Their energy position and intensity is a very sensitive function of the interatomic distance⁽²⁰⁾ and site symmetry. The effect of the symmetry on the intensity of the peak A is clearly observed in the spectrum of KMnO_4 . Also theoretically it has been demonstrated that transition to final states of t_2 symmetry, d-like, become partially allowed in tetrahedral symmetry⁽²¹⁾.

The peak D are due to more delocalized states and are more sensitive on the second shell effects. In fact they are very weak in the spectrum of the Mn^{2+} ion in solution and in the spectra of MnATP and MnAMP. On the contrary they appear clearly in the spectra of inorganic compounds like MnO and phosphates.

5.2. - Solid state effects.

We have found experimental evidence that solid state effects have to be considered to explain the XANES of simple oxides in Fig. 2. In fact the octahedral symmetry of the MnO_6 clusters in MnO and MnO_2 , is about the same, but the XANES are completely different, both concerning the number, intensity and relative energy position of the peaks. In the derivative spectra of Fig. 2, the structure A is splitted in three components in the MnO_2 spectrum while only one peak is observed in MnO. Large differences are also observed for the structures C and D. These differences in the spectra can be assigned to the different band

structure of the crystals. We cannot distinguish if the crystal periodicity is determinant or it is sufficient to take account of larger cluster which includes also the second and third shell. In the two compounds the second and third coordination shell around the Mn ions are completely different⁽²²⁾. The MnO₂ has only two Mn atoms at a 2.871 Å distance and four O⁻² at 3.34 Å. In comparison, MnO has twelve Mn atoms at 3.14 Å distance. Such a large asymmetry in the second shell may be responsible for the splitting of the structure A. Also the structures C and D, due to electronic transitions in the continuum, have largely different relative intensities, probably for the same reasons. So it seems that the molecular approach is not sufficient^(10, 17, 23, 29), and it is necessary to consider also the long range order to describe the final state wavefunction.

The effects of the second and third shell are clearly observed in the EXAFS part of the spectra of simple oxides. In Fig. 6 the modulating part $\chi(k)$ of the absorption coefficients of MnO₂ is plotted, and its Fourier transform is reported in Fig. 7. The amplitude of the peaks shows the contribution of neighbour shells. In Mn complexes only one peak is observed in the Fourier transform. The poor crystalline order in these compounds washes out the contribution of the second and third shells in the EXAFS spectra. Probably for the same reason also the XANES are determined only by the first neighbour shell in these compounds.

In the case of Mn₂O₃, which has a spinel structure, two different adjacent kinds of local structure with tetrahedral and octahedral symmetry are present. The tetrahedral sites are expected to give a very intense structure A, due to the allowed transition to the t₂ final molecular state like in KMnO₄. The fact that this strong peak A is not observed in Mn₂O₃ supports the idea that the final states of core transition in these compounds are delocalized. In conclusion we have found that in simple Mn oxides long range order is important for the final state wavefunction. Solid state effects have been already observed main

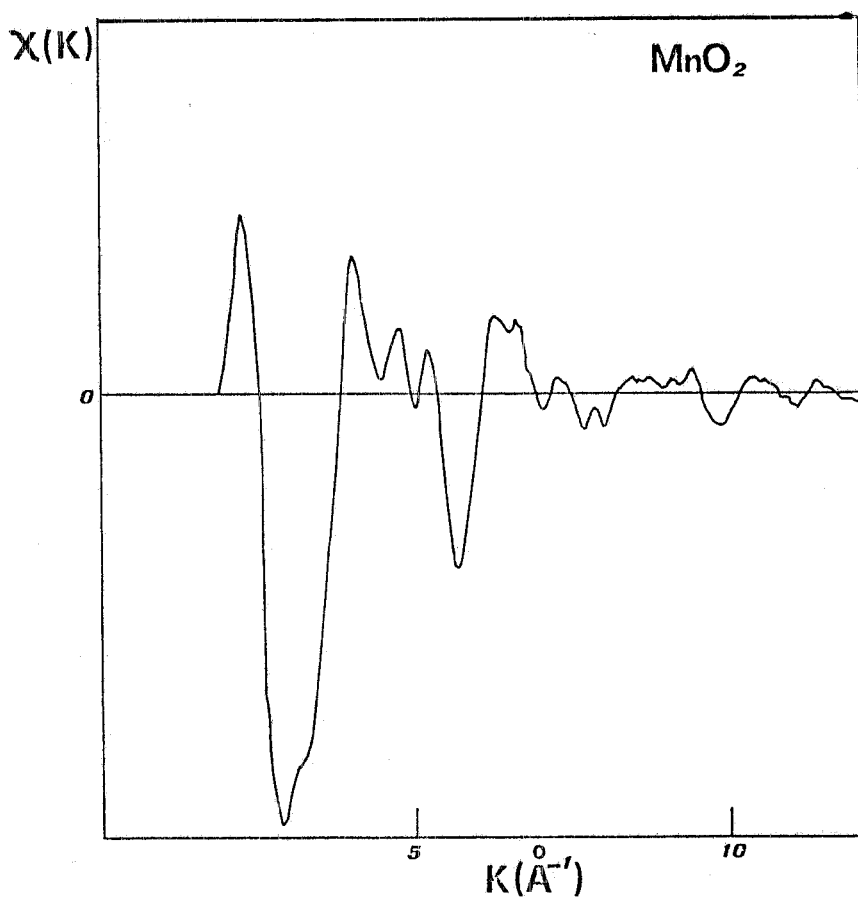


FIG. 6 - Modulating part $\chi(K)$ of the EXAFS spectrum of MnO_2 .

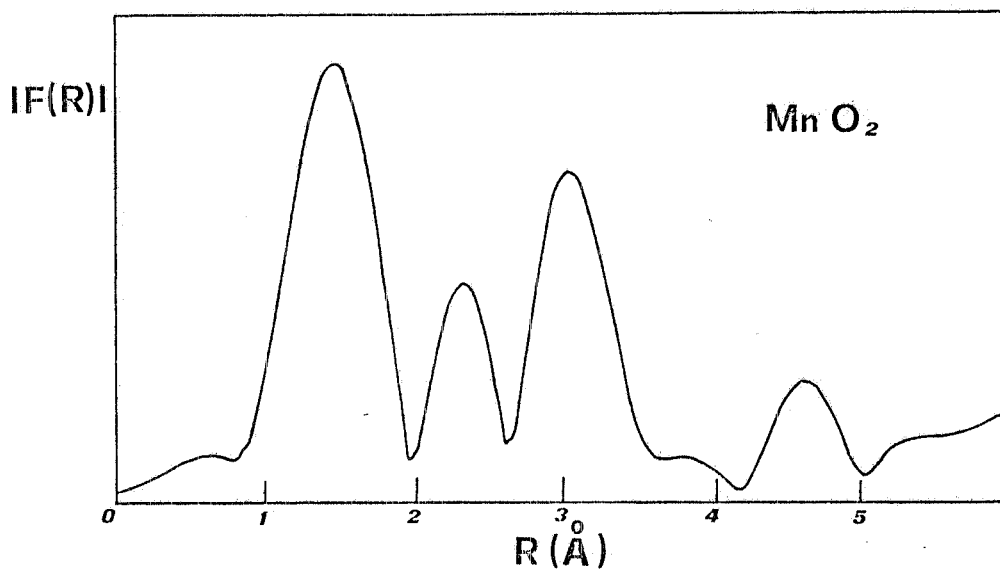


FIG. 7 - Fourier transform of $\chi(K)$ for MnO_2 EXAFS spectrum.

ly for metals where the spectra have been interpreted considering only the local density of states and selection rules⁽²⁴⁾. Such solid state approach has been proposed also for a simple cubic crystal like LiF⁽²⁵⁾ and molecular crystals like rare gas solids where the first peaks in core level spectra have been identified as core excitons⁽²⁶⁾.

5.3. - Chemical shift.

The chemical shift of the X-ray absorption edges has been correlated with the effective charge⁽³⁰⁾ on the absorbing Mn ion^(27, 28). In poor resolution absorption spectra taken by previous authors the "edge" is conventionally defined as the first derivative peak. Despite the fact that our high resolution spectra exhibit a large number of peaks, we have associated the absorption edge with peak B. In Fig. 8 the energy position of A, B, C peaks are reported as a function of the formal oxidation state of Mn ion. Concerning peak A, which is due to transitions to the final states of t_{2g} symmetry except for KMnO_4 , the energy shift is about linear but it is very small. The values of the energy shift of the B peak in the derivative spectra are scattered around an average straight line. The splitting of the peak B in Mn_2O_3 can be associated with the two different Mn sites in this compound giving rise to two different continuum threshold. We think that these plots show that not a simple relation⁽²⁷⁾ exists between the shift of the XANES and the effective charge on the Mn ion since the shift of the peaks is not determined only by the core level shift but also from the final state wave functions.

For example the peaks B and C of MnO are one below and the other above all other compounds with the same Mn valency and coordination number. A more physical quantity related with the chemical Mn-O bonding is the energy splitting of peaks B and C which is reported in Fig. 5. Their splitting is related with site symmetry and interatomic distance^(12, 18).

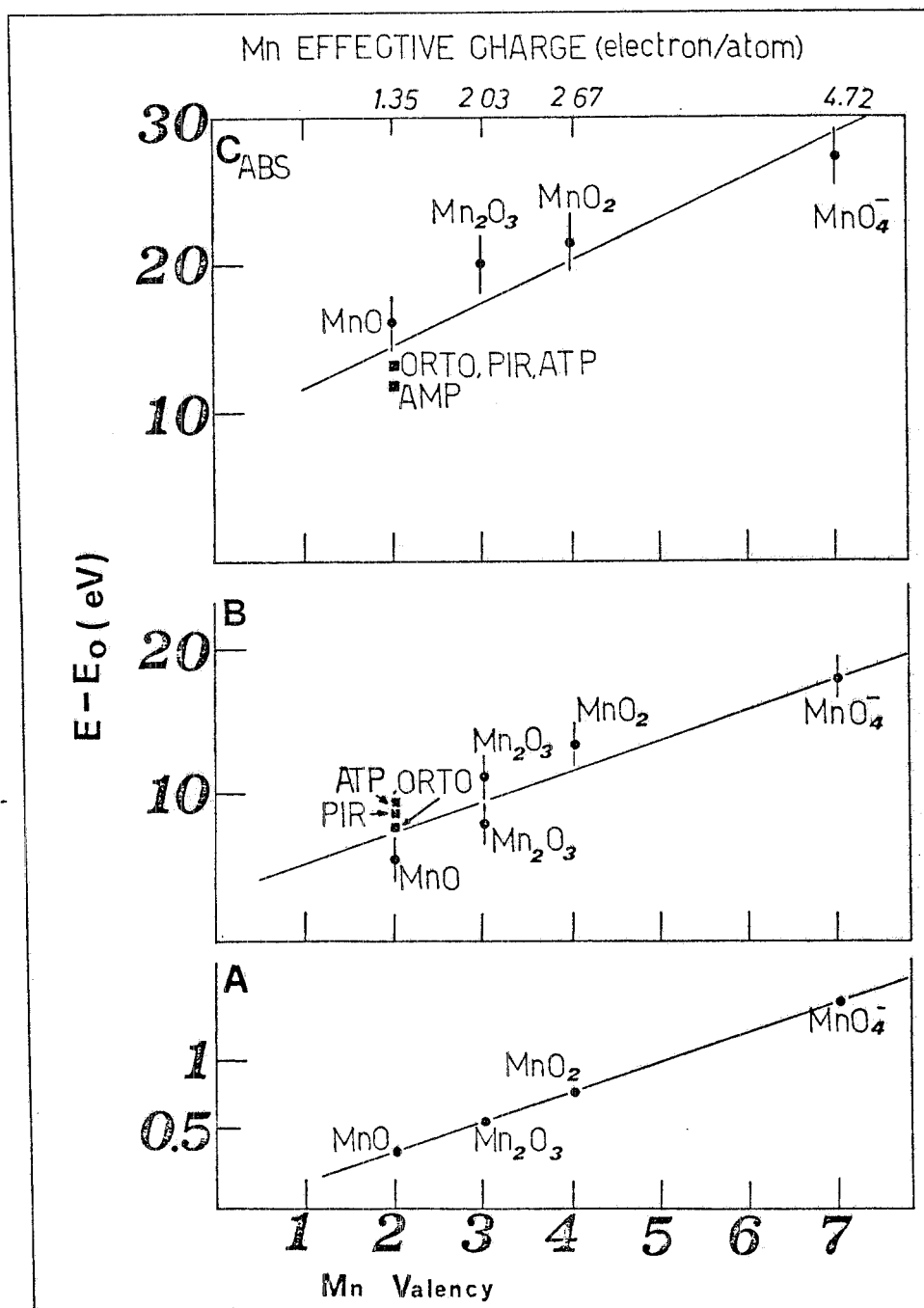


FIG. 8 - Energy position of A, B, C peaks vs. formal oxidation state of Mn ion. A, B are peaks in the derivative spectra reported in Figs. 2 and 3; C is the main peak of the absorption spectra of Fig. 1.

6. - CONCLUSIONS.

We have reported high resolution X-ray absorption spectra of Mn compounds. While molecular effects are enough to explain the XANES of complexes, solid state effects have to be taken into account in simple oxides spectra. The shift of the XANES is only qualitatively depending on the effective charge on the Mn ion. The splitting of the B-C peaks seems to follow the covalency of the Mn-O bonding.

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- (30) - The effective coordination charge η is given by

$$\eta = s - \sum_k n_k c_k$$

where s is the valency, the sum over k is intended to all the different kinds of neighbour ligands and c_k is the degree of covalence of a bond,

$$c_k = 1 - e^{-\frac{1}{4}(x_A - x_B)^2}$$

where x_A is the electronegativity.

In ref. (27), the following formula has been used

$$q = n \left\{ 1 - 0.01185 \left[\left(\frac{z}{r'} + \frac{z'}{r} \right) \right] \right\}$$

where z , r , n are the total number of electrons, the ionic radius, and the oxidation number of cations.

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