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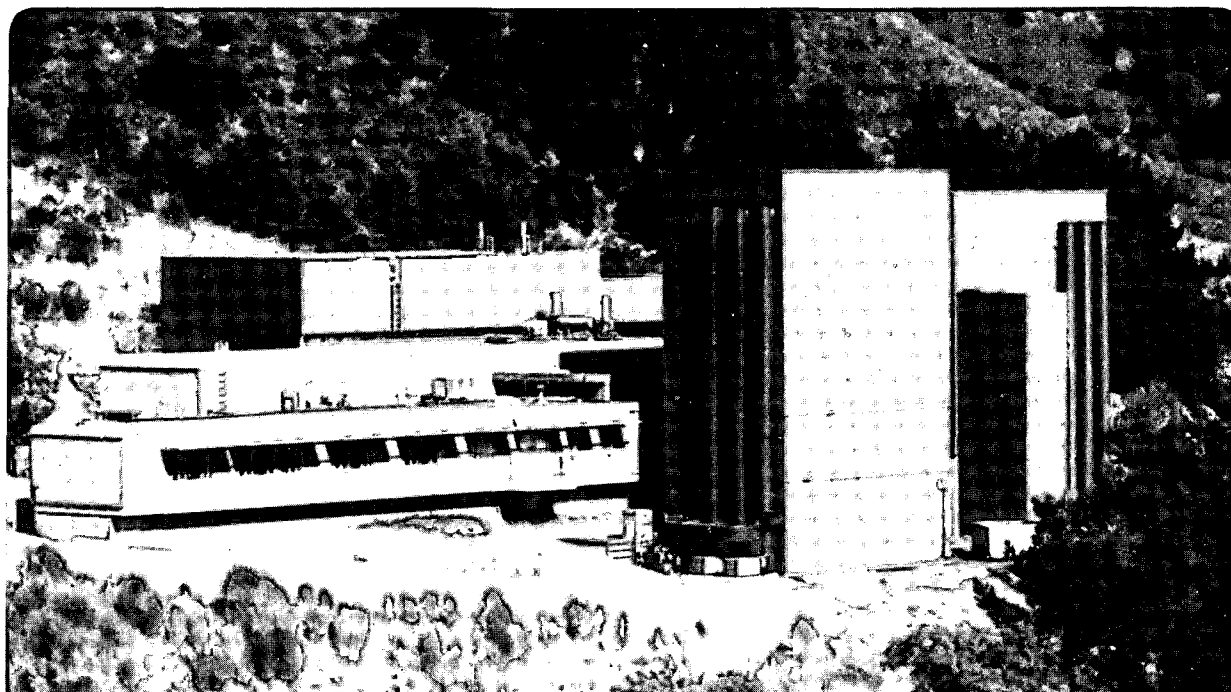
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Iron L<sub>3,2</sub> near edge fine structure studies

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## ABSTRACT

L<sub>3,2</sub> near edge fine structures of iron in different oxidation states and coordination numbers, measured with a parallel electron energy-loss spectrometer operating at 1.0-1.3 V resolution, show distinct splittings of the white lines. The splittings have been interpreted in terms of a simple atomic approach involving ligand field splitting of the d orbitals. It is shown that Fe(III) fine structure is particularly sensitive to its coordination.

## INTRODUCTION

The L<sub>3,2</sub> edges of the 3d transition metals, observed in either x-ray absorption or electron energy-loss spectroscopy are marked by prominent features at the threshold called "white lines". These features are due to excitations of the electrons from the 2p<sub>3/2</sub> and 2p<sub>1/2</sub> spin orbit split levels to the unoccupied 3d levels. L<sub>3</sub>/L<sub>2</sub> ratios for a variety of transition metals and their oxides/complexes have been measured and shown to be a function of the oxidation state [1-3].

Fine structures of the L<sub>3,2</sub> white lines have been interpreted either by multiconfiguration Dirac-Fock calculations of the transition rates including many-electron effects [4] or by a systematic linear augmented plane wave calculation [5]. Alternatively, as the 3d electrons of the transition metal compounds are localized, it is possible to interpret these structures either in terms of multiplet splitting involving the interactions of the 2p core hole and unpaired 3d electrons of a localized metal ion [6,7] or due to crystal field effects[8,9]. Even though the origin of the details of the different edge features is not well understood, the technique can be used to probe the geometrical and electronic structure of a metal site. This paper discusses the results of an experimental investigation of the near edge fine structure of four model oxide minerals containing iron in specific oxidation state and coordination. A simple atomic approach invoking ligand field splitting of the d levels has been found to adequately describe our observations.

## EXPERIMENTAL

Electron energy-loss spectra were collected using a Gatan 666 spectrometer with parallel recording and a JEOL 200CX transmission electron microscope operating at 120kV. The energy resolution was between 1.0 and 1.3 eV. All spectra were acquired in image mode with an energy dispersion of 0.1V per channel, a beam divergence of 3.5 mrad and a spectrometer entrance aperture subtending an angle of 13.5 mrad.

Four different mineral samples, each containing iron in a specific oxidation state and coordination, were investigated. They were franklinite (nominal composition  $[\text{Zn}, \text{Mn}]\text{Fe}^{3+}_2\text{O}_4$ ) where Fe(III) is in octahedral sites; hercynite (nominal composition  $\text{Fe}^{2+}\text{Al}_2\text{O}_4$ ) where Fe(II) is in tetrahedral sites; fayalite (nominal composition  $\text{Fe}_2\text{SiO}_4$ ) where Fe(II) is in octahedral coordination; and an iron analogue of leucite (nominal composition  $\text{KFeSi}_2\text{O}_6$ ) where Fe(III) is in tetrahedral coordination.

## RESULTS & DISCUSSION

Figures 1a and b show the  $L_3/L_2$  edges for Fe(III) in octahedral and tetrahedral coordination respectively. In the former case, both the  $L_3$  and  $L_2$  edges show distinct splittings, separated by 1.6eV, at the onset of the edge. No such splitting is observed in the latter. Figures 1c and d show the  $L_3$  and  $L_2$  edges for Fe(II) in octahedral and tetrahedral sites. The  $L_3/L_2$  peak height ratio is lower for Fe(II) compared to Fe(III), in agreement with earlier observations. The  $L_3$  and  $L_2$  edges for Fe(II) in octahedral coordination is a single peak with a slight broadening.

The observed fine structures can be interpreted in terms of a simple ligand field approach [8]. Figure 2 shows the ligand field splitting of the d orbitals for the two different coordinations and the distribution of the Fe electrons in these levels. The commonly observed low spin state for iron in all these cases has been assumed. In consistence with ligand field theory the splitting for the tetrahedral coordination is drawn smaller than for the octahedra. For Fe(III) in octahedral coordination, in addition to the empty  $e_g$  levels there is an unpaired electron in the  $t_{2g}$  level. This explains the splitting of the  $L_3$  and  $L_2$  white line features in Figure 1a. For Fe(III) in tetrahedral coordination, the energies of the ligand field split levels,  $e_2$  and  $t_2$ , are reversed. The lower  $e_2$  level is completely filled and therefore one observes a single peak (fig. 1b). In addition, the leucite structure is known to exhibit some tetragonal distortion. Such a distortion would give rise to a further splitting of the triply degenerate  $t_2$  levels and explain the small broadening observed. For Fe(II) in octahedral coordination, the six available electrons completely occupy the doubly degenerate  $e_2$  level. The spectrum for Fe(II) in tetrahedral coordination exhibits a pronounced splitting of  $L_3$  edge. The additional feature is observed at an offset of 1.8eV towards higher energies. It is well known that in hercynite considerable substitution of  $\text{Fe}^{3+}$  for Al may occur.

The above observation (Fig. 1d) is consistent with the the expected chemical shift for Fe(III).

In addition to the above, substantial variation in the fine structure of the oxygen K edges is also observed. A detailed interpretation of these fine structures in their entirety is in progress and will be published shortly. However, in this short communication we would like to emphasize the applicability of an atomic approach to the interpretation of 'white line' fine structures. The ability to resolve the effects of oxidation state and the coordination in these oxides should find application in understanding the magnetic behaviour of a wide range of magnetic oxides.

#### ACKNOWLEDGEMENTS

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## FIGURES

1.  $L_3$ ,  $L_2$  edges of iron in the four different compounds: (a) Fe(III) in octahedral coordination, (b) Fe(III) in tetrahedral coordination, (c) Fe(II) in octahedral coordination and (d) Fe(II) in tetrahedral coordination. In (d) the splitting of the  $L_3$  edge is due to the chemical shift of Fe(III).
2. A simple ligand field interpretation of the Fe  $L_3$  and  $L_2$  edges observed in Fig. 1.



# OCTAHEDRAL

# TETRAHEDRAL

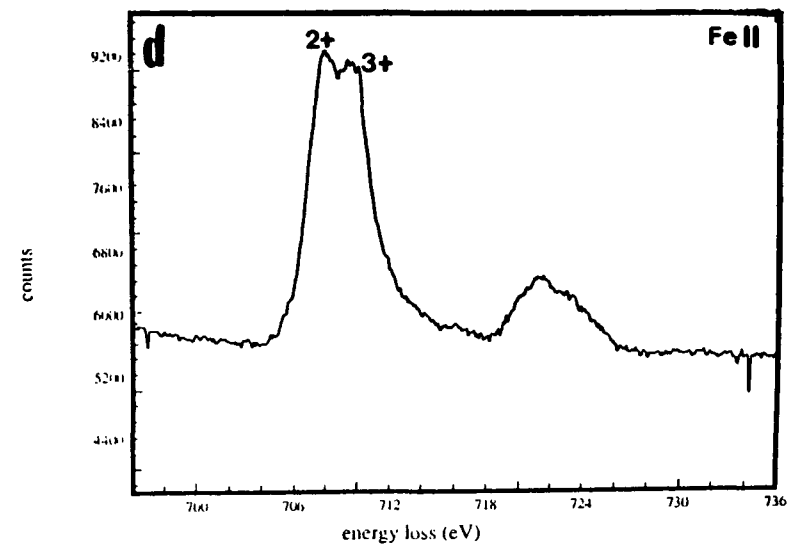
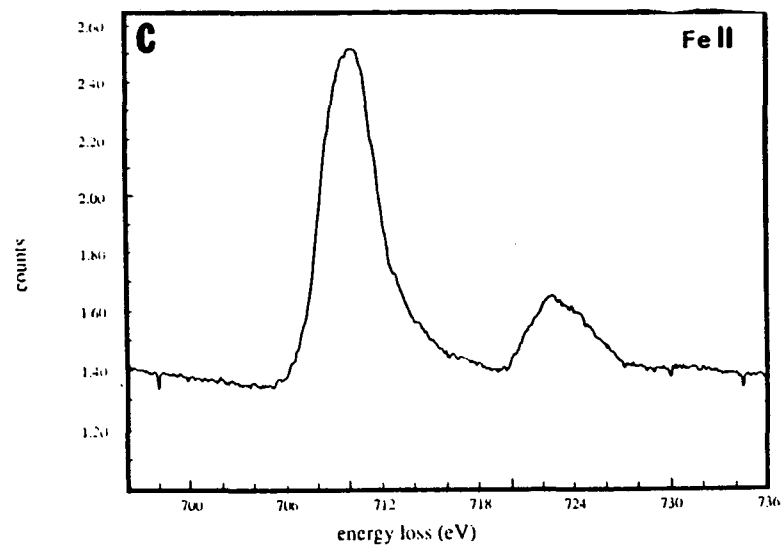
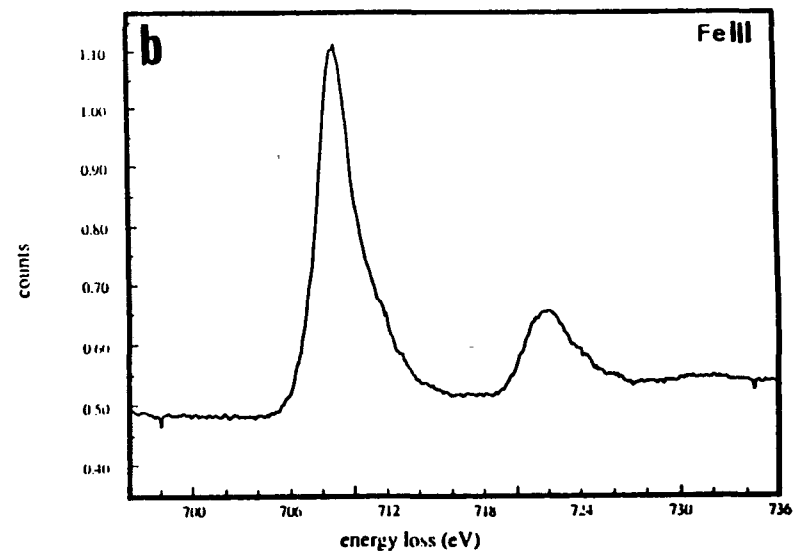
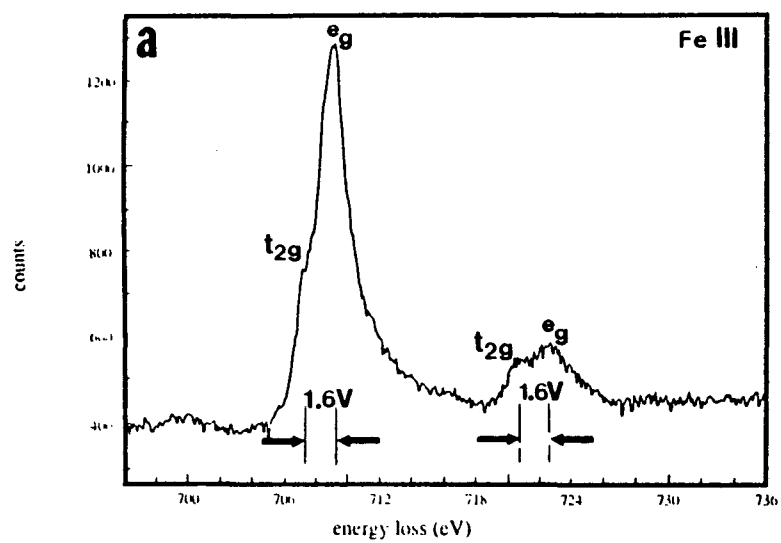


Figure 1

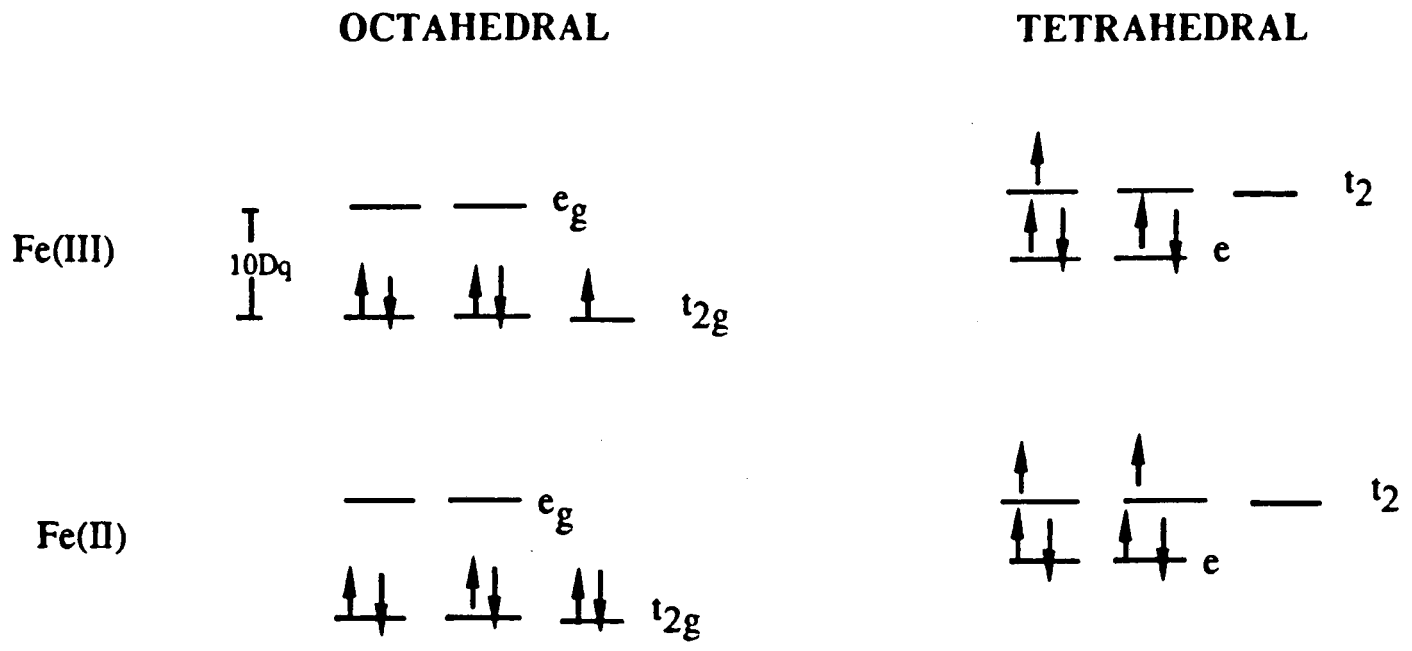


Figure 2

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