THE AMERICAN MINERALOGIST, VOL. 56, JULY-AUGUST, 1971

INVESTIGATIONS OF THE $L_{II,III}$ X-RAY EMISSION SPECTRA OF Fe BY ELECTRON MICROPROBE. PART 2. THE Fe $L_{II,III}$ SPECTRA OF Fe AND Fe-Ti OXIDES

R. K. O'NIONS[1] AND D. G. W. SMITH, *Department of Geology, University of Alberta, Edmonton, Alberta*

ABSTRACT

The Fe $L_{II,III}$ X-ray emission spectra of Fe and Fe-Ti oxides have been investigated at operating voltages between 2.0 and 30.0 kV using an electron probe. The L_{II} band is due to transitions from antibonding and the L_{III} band from both bonding and antibonding molecular orbitals. After absorption corrections are applied the L_{II}:L_{III} integrated intensity ratios increase with operating voltage (e.g., for wustite $L_{II}/L_{III}=2.5$ at 30.0 kV). These features are discussed in terms of higher transition probabilities from bonding molecular orbitals to O_{1s} than to Fe $_{2p}$. L_{II} and L_{III} intensities per unit concentration of Fe are higher in Fe^{2+}-oxides than in more covalent Fe^{3+}-oxides and are further enhanced by the presence of Ti^{4+}. At the present time it does not appear possible to gain more than qualitative information concerning Fe^{2+}:Fe^{3+} ratios in more complex minerals by measurement of L_{II}:L_{III} ratios.

INTRODUCTION

Recent preliminary investigations of the Fe $L_{II,III}$ X-ray emission spectra of various oxides and silicates, containing both divalent and trivalent iron, (Andersen, 1967; Albee and Chodos, 1969, 1970) have aroused interest in the possibility of determining the oxidation state of Fe in a wide range of minerals using the electron microprobe. Presently, however, insufficient information is available concerning the effects of absorption and chemical combination for the techniques to be of general applicability.

In the first paper of this series, Smith and O'Nions (1971) have shown that in the range of operating voltages between 2.0 and 30.0 kV absorption corrections can be applied to the L_{II} and L_{III} integrated intensities of Fe-metal to give an L_{II}:L_{III} ratio close to 0.5. The present paper extends this work to Fe and Fe-Ti oxides with a view to obtaining information concerning the relative influences of oxidation state and chemical combination on the Fe $L_{II,III}$ spectrum.

The Fe $L_{II,III}$ spectra of hematite (Fe_2O_3), wustite ($Fe_{1-x}O$), ilmenite ($FeTiO_3$), goethite ($HFeO_2$) and pseudobrookite (Fe_2TiO_5) have been investigated. In these compounds Fe is in the high spin state, therefore Fe^{3+} has a $(t_{2g})^3$, $(e_g)^2$ and Fe^{2+} a$(t_2g)^4$, $(e_g)^2$ configuration. In first series transition metal compounds $3d$ electrons, when present, are involved in

---

[1] Present address: Department of Geology and Mineralogy, University of Oxford, Parks Road, Oxford. U.K.

bond formation with ligands and the usual concept of the L_{III} ($\equiv L\alpha_{1,2}$) band arising from an $L_{III} \leftarrow M_{IV,V}$ transition and the L_{II} ($\equiv L\beta$) band from an $L_{II} \leftarrow M_{IV}$ transition is not entirely applicable. It is necessary in any discussion of L X-ray spectra of such compounds, to consider not only the nature of the ligands, but also the extent of electron delocalization together with stereochemical factors. Molecular orbital theory is undoubtedly the most applicable in such cases and results presented herein will be discussed within this framework. It should be noted that Glenn and Dodd (1968) and Dodd and Glenn (1968, 1969) have interpreted features of K-emission and absorption spectra of Mg, Al, and Si using molecular orbital theory, and Urch (1970) has offered a molecular orbital interpretation of low energy satellite lines in some emission spectra.

Fischer (1965) investigated the $L_{II,III}$ X-ray emission spectra of some first series transition metals and their oxides. Pertinent to the present discussion are his investigations of the Fe $L_{II,III}$ band intensities of Fe-metal, Fe_2O_3, and Fe_3O_4 at excitation voltages between 1 and 8 kV; the $L_{II}:L_{III}$ intensity ratios were found to be considerably higher for Fe_2O_3 and Fe_3O_4 than for the metal. Bonelle (1966) in a comprehensive study of $L_{II,III}$ emission and absorption spectra of first series transition metals and their oxides has discussed in detail the $L_{II,III}$ spectra of Fe-metal and Fe_3O_4 under conditions of differing self absorption.

Recently Albee and Chodos (1970) have made numerous measurements of Fe $L_{II}:L_{III}$ intensity ratios in oxides and silicates at an operating voltage of 15 kV. Although no attempt was made to apply absorption corrections, there does appear to be a distinct relationship between Fe-oxidation state and the $L_{II}:L_{III}$ ratio; this is particularly clear for the hematite-ilmenite and the magnetite-ulvöspinel series. Possible reasons for the less distinct relationships noted in more complex solid solutions will be discussed later.

EXPERIMENTAL

All measurements reported here were performed using an ARL-EMX electron microprobe. A detailed description of experimental procedures employed to measure the integrated peak intensities and correct for overlap of the L_{II} and L_{III} bands, together with details of pulse height discrimination of high order Fe K lines, have been given by Smith and O'Nions (1970).

With the exception of pseudobrookite, sufficiently large samples were available to use a somewhat defocussed beam ($\simeq 20\mu m$), whilst the specimen was driven continuously at 96 $\mu m/min$; in this way significant surface contamination and specimen damage, from the 1 μA to $3\mu A$ beam currents commonly utilized, were avoided. The small size of the pseudobrookite grains necessitated the use of a more focussed beam ($\simeq 5$ μm), beneath which the specimen was moved at frequent intervals. Spectra for hematite obtained at 2, 5, and 20 kV afford examples of the general character of the Fe $L_{II,III}$ emission from oxides (Fig. 1).

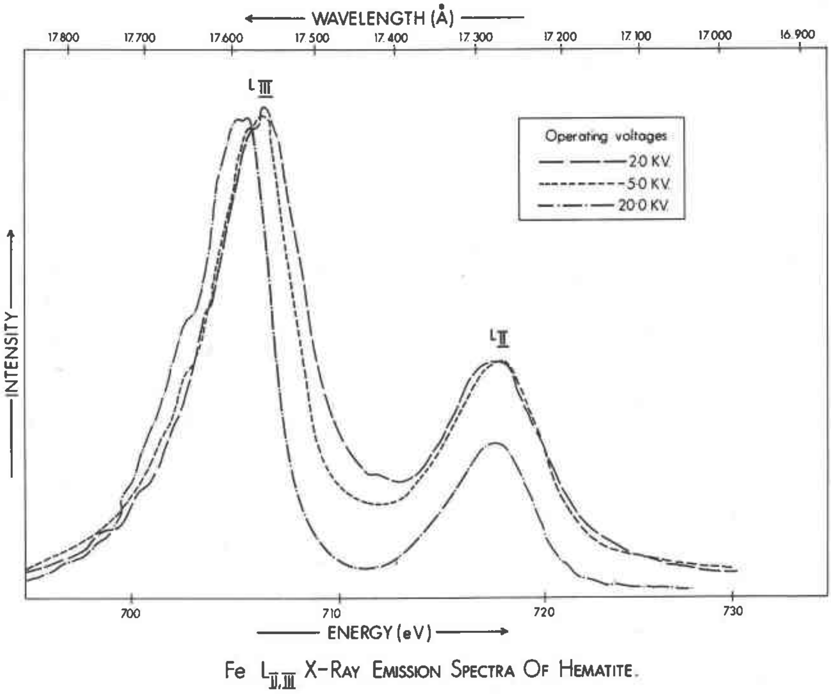

FIG. 1. Sample Fe $L_{\mathrm{II,III}}$ spectra for hematite at 2, 5, and 20 kV, showing detailed shapes of L_{II} and L_{III} bands based on step counting of intervals of 0.003 Å.

These spectra were obtained by stepping at intervals of 0.003 Å and counting for periods of 100 to 200 secs. (depending on the counting rate) at each position.

THE FE $L_{\mathrm{II,III}}$ SPECTRUM

Because the L_{III} absorption edge lies between the L_{II} and L_{III} bands, the latter undergo differential self-absorption; the most obvious effects of which are the reduction of L_{II} relative to L_{III} intensity at higher operating voltages and an *apparent* shift of the L_{III} peak to lower energy with increasing kV. This shift has been attributed to a greater absorption of the high energy side of the band relative to the low energy side (Smith and O'Nions, 1971). Such differential self-absorption has a marked effect on the apparent band width at half-peak maximum (5.8 eV at 2 kV and 4.9 eV at 20 kV) and emphasises the necessity for making band width measurements from spectra obtained under conditions of negligible self-absorption (not possible with the electron probe). Alternatively measurements of the band width at several operating voltages could be made and extrapolated to the critical excitation voltage for the Fe L spectrum, where absorption effects are zero. Spectral resolution was insufficient to resolve unambiguously satellite peaks on the high energy sides of the L_{II} and L_{III} bands observed by other workers (*e.g.* Fischer, 1965) using more specialised equipment. It does seem possible, however, to detect a doublet comprising the main L_{III} peak and a second, poorly resolved peak, on the low energy side of the band. These peaks may be due to transitions from different molecular orbitals and will be further discussed later.

VARIATION IN L_{II}:L_{III} RATIO

In the case of Fe-metal Smith and O'Nions (1971) have shown that erroneous values for the L_{II}:L_{III} ratios are obtained by simple measurement of peak heights, but that this difficulty may be overcome by making integrated intensity measurements. Such measurements were made for hematite, goethite, wustite, ilmenite, and pseudobrookite (see Appendix for composition of materials). The variation in L_{II}:L_{III} ratio with operating voltage for these oxides is quite different from that for Fe-metal (Fig. 2); each oxide shows an initial increase in the ratio and then a decrease at high kV. These variations would not be expected from differential absorption effects alone (*cf.* Fe-metal). By extrapolation of the L_{II}:L_{III} ratios to the critical excitation voltage for the Fe L spectrum ($\simeq$0.7 kV), where absorption corrections should be zero, values around 0.5 are obtained, with the notable exception of that for wustite, which is somewhat lower.

Absorption corrections to the oxide data are made difficult not only by the uncertainty regarding the best formula to use at long wavelengths, but also by uncertainties in the mass absorption coefficients. The situation is further complicated by possible differences in energy distribution within the L_{III} bands of different oxides relative to the position of the L_{III} absorption edge. Smith and O'Nions (1971) applied several absorption correction formulae in current usage to the Fe-metal data and concluded that Heinrich's (1967) formula, with mass absorption coefficients calculated from Kelly (1966), gave the most consistent results, although they were still not entirely satisfactory. Since the mass absorption coefficients of the oxides for L_{II} and L_{III} have more similar values, and uncertainties in their values should have less influence on the corrected L_{II}:L_{III} ratio, it was felt justifiable to apply the correction to the oxide data.

Absorption corrected L_{II}:L_{III} ratios for the oxides are compared with those for Fe-metal in Figure 3. Application of the correction results in a smooth variation of the L_{II}:L_{III} ratio with operating voltage, marked in each instance by an overall increase of the ratio. The increase is most extreme for wustite (L_{II}:L_{III} ratio of 2.5 at 30 kV) and least for pseudobrookite (0.8 at 30 kV). In view of the limitations imposed by absorption

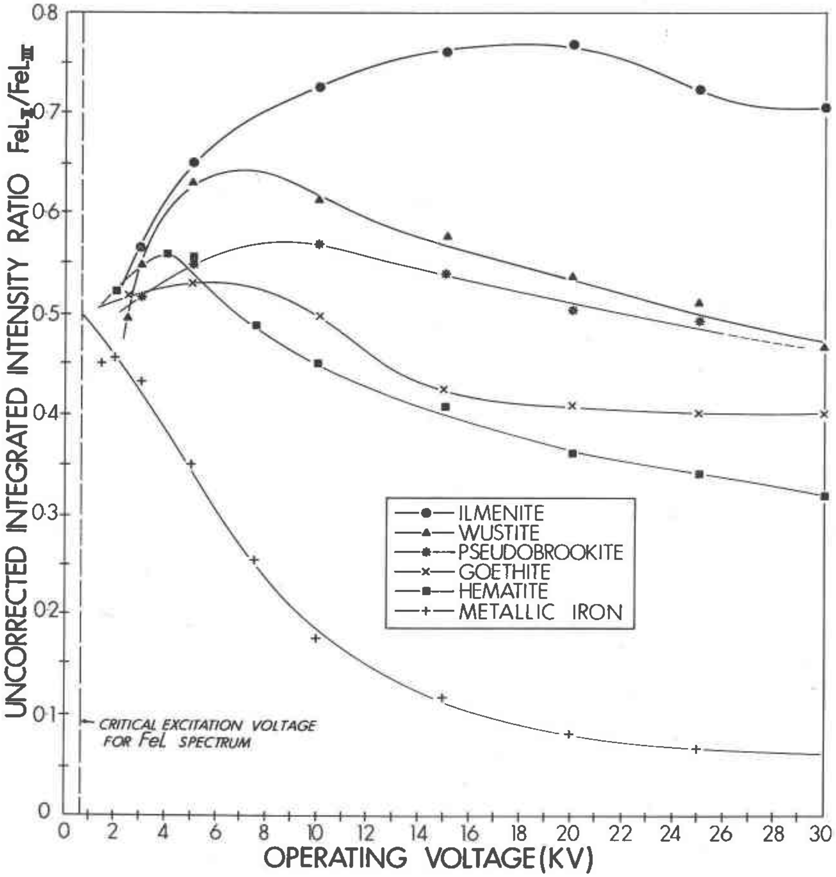

FIG. 2. Integrated Fe L_{II}:L_{III} intensity ratios from 2.0 to 30.0 kV for hematite, wustite, goethite, ilmenite, pseudobrookite, and Fe-metal.

correction uncertainties mentioned above it should be re-emphasised that only qualitative, or at the best semiquantitative, comparisons of the results are possible.

Of interest are the extrapolated L_{II}:L_{III} ratios of the corrected curves to the critical excitation voltage of the Fe L spectrum, (Fig. 3). The lowest extrapolated intercept is for wustite (ratio of 0.32) and this also has the steepest initial rate of increase, whereas the other Fe^{2+} compound, ilmenite, intercepts at 0.42 and has an intermediate slope. The three Fe^{3+} compounds (hematite, goethite, and pseudobrookite) have very similar intercepts (approximately 0.47) and generally lower slopes than the Fe^{2+} compounds. These extrapolated intercepts bear little resemblance to the ratios measured at higher operating voltages.

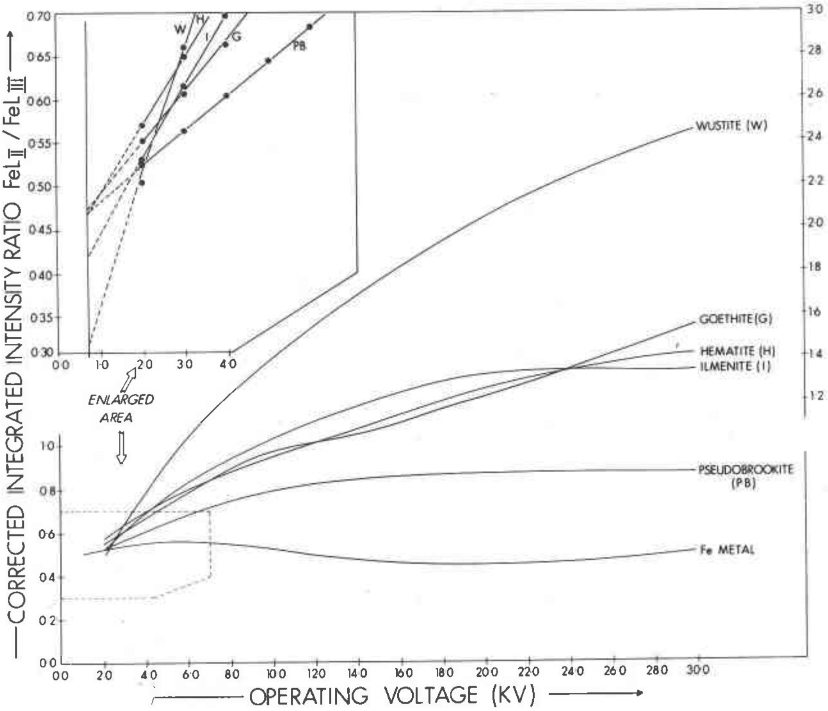

FIG. 3. Absorption corrected Fe $L_{II}:L_{III}$ integrated intensity ratios for hematite, wustite, goethite, ilmenite, pseudobrookite, and Fe-metal using Heinrich's (1967) formula and Kelly's (1966) mass absorption coefficients. Extrapolation of corrected ratios to critical excitation voltage for Fe L spectrum inset (N.B. data points are values read from corrected curves).

Further comparisons of the L_{II} and L_{III} band intensities have been carried out at 15 kV and all normalised to a beam current of $1\mu A$ (Table 1). Measured values were corrected for absorption as described previously, the same limitations applying. The values quoted are an expression of the relative radiation intensities per unit concentration of Fe. The L_{II} and L_{III} values for goethite and hematite are similar and those for wustite somewhat higher. Both of the Ti-bearing minerals, *i.e.* ilmenite and pseudobrookite, have considerably higher values.

DISCUSSION

There is now much evidence suggesting that upon band formation electrons are partially delocalised into molecular orbitals (see reviews by Gray, 1964 and Mitchell, 1969). Interpretation of features of L X-ray spectra of first series transition metal compounds in terms of molecular orbital theory therefore are undoubtedly more realistic than earlier

TABLE 1. RELATIVE INTENSITIES OF Fe L_{II} AND L_{III} RADIATION PER UNIT CONCENTRATION OF Fe AT 15kV

Oxides	L_{III}/atom[a]	L_{II}/atom[a]
Fe-oxides		
Hematite (Fe_2O_3)	3.70	3.60
Goethite (FeOOH)	3.80	4.00
Wustite ($Fe_{1-x}O$)	5.70	9.00
Fe-Ti oxides		
Pseudobrookite (Fe_2TiO_5)	13.50	11.40
Ilmenite ($FeTiO_3$)	12.60	15.20

[a] Units arbitrary.

interpretations. General introductions to molecular orbital (MO) theory have been given by Ballhausen and Gray (1964), and Cotton and Wilkinson (1966). Introductions pertinent to first series transition metals may be found in Gray (1964) and Burns (1970).

In each of the oxides under consideration Fe is hexacoordinated with oxygen. The coordination polyhedron around Fe possesses approximately O_h symmetry, however in pseudobrookite the octahedra are severely distorted towards tetrahedral symmetry (Pauling, 1930). Although the stereochemistry differs in detail, particularly in pseudobrookite, it is sufficient for the present purposes to discuss aspects of the Fe $L_{II,III}$ spectra in terms of molecular orbitals consistent with O_h symmetry. Molecular orbitals are shown for a $3d^6$ compound in Figure 4; it should be noted that the relative orbital energies are only approximate and if the required computations were performed would be modified somewhat. The separation 'Δ' between $t_{2g}\pi^*$ and $e_g\sigma^*$ corresponds to the crystal field splitting parameter of crystal field theory and this will be somewhat different for $3d^5$ compounds. On the basis of energy considerations one might expect the bonding molecular orbitals (BMO) to be largely comprised of O $2p$ orbitals and the antibonding molecular orbitals (ABMO) of Fe $3d$ orbitals.

It was noted earlier that the L_{III} band of hematite (Fig. 1) has three distinguishable components—a poorly resolved low energy peak between 3 and 5 eV lower in energy than a main L_{III} doublet. These components are also distinguishable in the L_{III} band of Fe_3O_4 reported by Bonelle (1966). The BMO's and ABMO's having the required symmetry for dipole radiation are the $e_g\sigma^b$, $t_{2g}\pi^b$, $e_g\sigma^*$, and $t_{2g}\pi^*$. The poorly resolved low energy peak may then be assigned to a transition from $e_g\sigma^b$ and/or $t_{2g}\pi^b$ and the doublet to transitions from $t_{2g}\pi^*$ and $e_g\sigma^*$. The L_{II} band width for Fe_3O_4 obtained by Bonelle (1966) under conditions of lower self absorption than our spectra, is approximately half that of L_{III},

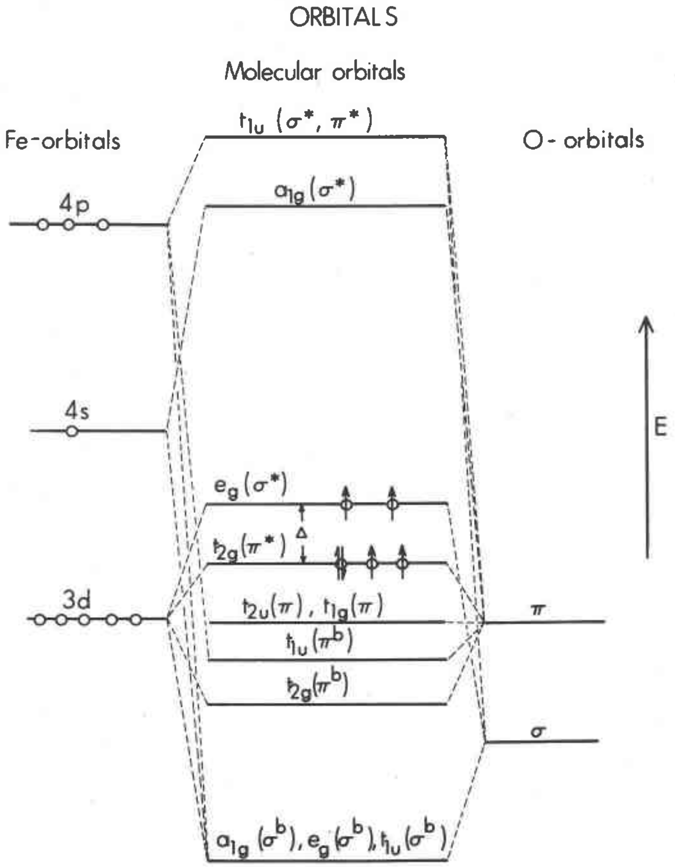

FIG. 4. Qualitative moleculor orbital energy level diagram for octahedrally coordinated Fe^{2+} (O_h symmetry). Electron distribution between antibonding orbitals indicated.

which may indicate that the L_{II} band arises from transitions from antibonding orbitals alone. If the *assumption* is made that the L_{II} band is due to transitions from ABMO's and the L_{III} band to transitions from both BMO's and ABMO's certain aspects of the $L_{II}:L_{III}$ intensity variation in oxides may be easily explained.

It is clear that some factor tends to enhance L_{II} or deplete L_{III} with increasing operating voltage for all of the oxides studied. Since *O 2p* electrons are delocalised into molecular orbitals the O $K\alpha$ and Fe L_{III} bands may partially arise from BMO's of the same wave function; the extent to which this is the case depends on the amount of covalent bond character. The data of Reed (1965) concerning relative intensities of so-called 'comparable' K and L lines indicates that the intensity of L_{III}

should be considerably less than the $K\alpha$ intensity. This together with the BMO's having *far more* ligand than metal character might imply that the transition probability from a given BMO, which would be involved in both the production of the Fe L_{III} band and the O K band, to the 1s orbital of oxygen should be greater than that to the 2p orbitals of Fe. One can therefore anticipate the increase in $L_{II}:L_{III}$ ratios with operating voltage. These effects are shown schematically in Figure 5. The marked tendency for the $L_{II}:L_{III}$ ratio to level off at higher operating voltages (Fig. 3) may be in part attributable to the stopping power factor of the atomic number effect, which would progressively enhance the probability of ionizing oxygen rather than iron. Additional evidence for part of the L_{III} band arising from transitions from BMO's in some first transition metal oxides comes from the work of Fischer and Baun (1968). These authors assigned the main peak in Ti-oxides to a symmetry forbidden 'crossover' from metal to ligand of the $p \rightarrow p$ type and suggest that under certain conditions selection rules may be relaxed to allow such a transition. Support for such a concept was derived from the similarity in form of the Ti L_{III} band and the O K band. However, the necessity for such

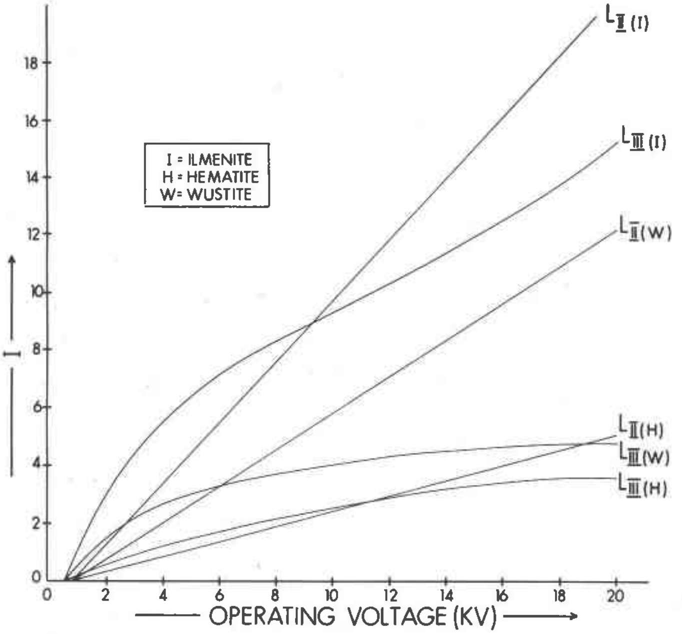

FIG. 5. Schematic diagram showing relative intensities (I: arbitrary units) of Fe L_{II} and L_{III} bands for wustite, hematite, and ilmenite assuming linear increase of L_{II} band intensity with operating voltage.

transition is removed in the preferable concept of partial electron delocalization and formation of molecular orbitals.

Absorption corrected L_{II} and L_{III} band intensities (Table 1) at 15 kV present some interesting features. Firstly, wustite has higher L_{II} and L_{III} band intensities per unit concentration of Fe than hematite and goethite, indicating a relative increase in intensities in the more ionically bonded compound, and secondly both ilmenite and pseudobrookite have higher band intensities than the Fe-oxides. The band intensities for ilmentite are higher than those for pseudobrookite showing the same relationship to Fe-oxidation state as do hematite and wustite. Since the Fe^{2+}-O bond is more ionic than the Fe^{3+}-O bond the amount of ligand character in the ABMO's of FeO should be less than in Fe_2O_3. This factor together with the additional t_{2g} electron in Fe^{2+} should increase the transition probabilities from the ABMO's (in wustite) to Fe L_{II} and L_{III} relative to hematite. Further, if the L_{II} band arises from an $L_{II} \leftarrow t_{2g}\pi^*$ transition, the rate of increase of intensity of the L_{II} relative to the L_{III} band may be faster for wustite than for hematite (Fig. 5). Ti^{4+} has a greater bond strength to oxygen than Fe^{2+} or Fe^{3+} and possibly this results in a more ionic character of the Fe-O bond in pseudobrookite and ilmenite than in the Fe-oxides, consequently increasing the transition probabilities from ABMO's.

CONCLUSIONS

Investigation of the Fe L_{II}–L_{III} spectra of Fe and Fe-Ti oxides has provided a basis for understanding the relative effects of oxidation state and chemical combination on the $L_{II}:L_{III}$ intensity ratios measured at various operating voltage. Certain features of the $L_{II,III}$ spectrum from Fe and Fe-Ti oxides, and variations in the $L_{II}:L_{III}$ ratio with operating voltage and bond character, can be understood in terms of molecular orbital theory. Because these latter effects are related to the Fe-oxidation state the $L_{II}:L_{III}$ ratios may be used to infer the $Fe^{2+}:Fe^{3+}$ ratios in simple solid solution series such as hematite-ilmenite and magnetite-ulvöspinel, as shown by Albee and Chodos (1970). However, in these circumstances little is to be gained from such a procedure since the Fe-oxidation state may be deduced from straightforward analysis and the assumption of stoichiometry. In the more complex solid solutions, such as micas and amphiboles investigated by Albee and Chodos (1970), less straightforward relationships could now be anticipated. For example in the case of calcic amphiboles the substitution of Ti^{4+}, and other coupled substitutions which may accompany $Fe^{2+}:Fe^{3+}$ variations, will have differing bond character and may greatly influence the measured $L_{II}:L_{III}$ ratios. For example, investigations of a suite of calcic amphiboles by the present authors (unpublished) have shown a marked dependence of the L_{II}:L_{III} ratio on Fe/Mg. At the present time there would appear to be little hope of gaining quantitative information concerning the oxidation state of Fe using techniques currently available. However, by further study of the Fe $L_{II,III}$ spectrum in more complex solid solutions it may prove possible to make allowances for some of the effects discussed above and to obtain at least semi-quantitative information on Fe^{2+}:Fe^{3+} ratios. At the same time interesting qualitative information can be gained concerning the nature of bonding by studies of Fe L spectra.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. R. G. Burns, Department of Geology and Mineralogy, Oxford, and Drs. T. Haas and M. J. Bennett, Department of Chemistry, Alberta, for useful discussions. Dr. G. Biggar, Grant Institute, Edinburgh kindly prepared the wustite sample. Valuable technical assistance in the microprobe laboratory was provided by Mr. D. A. Tomlinson. Financial support for the project was furnished by the National Research Council of Canada.

APPENDIX

TABLE 2. ANALYSES OF SAMPLES

	1	2	3	4	5
Si	0.10	n.f.	n.f.	n.d.	1.37
Ti	24.69	< 0.04	28.73	n.d.	n.f.
Al	3.82	< 0.03	n.f.	0.01	0.20
Fe^{3+}	32.32	69.84[a]	7.20	—	59.11
Fe^{2+}	3.65	—	31.81	76.26	—
Mn	trace	n.f.	0.25	n.d.	0.34
Mg	0.57	< 0.03	0.62	n.d.	0.04
O	35.32	30.06	31.89	23.70[b]	37.81[b]
Others	—	—	—	0.03[c]	1.13[d]
	100.47	100.00	100.50	100.00	100.00

n.f. Sought but not found; n.d.—not determined;

[a] Fe^{3+} by difference.

[b] Oxygen by difference.

[c] Pt.

[d] assumed H.

1. Pseudobrookite (Smith, 1965, table 9, P. 2007).
2. Hematite, Elba, Italy; multiple microprobe analyses of trace constituents.
3. Ilmenite, Ödegaarden, Norway. Electron microprobe analysis, stoictrometry assumed.
4. Synthetic wustite; microprobe analysis *vs.* Elba hematite.
5. Goethite (locality unknown); well crystallised material, microprobe analysis.

REFERENCES

ALBEE, A. A., AND A. CHODOS (1969) Semiquantitative electron microprobe determination of Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} in oxides and silicates and its application to petrologic problems. *Proc. 4th Nat. Conf. Electron Microprobe Analysis.* (Pasadena)

——— AND ——— (1970) Semiquantitative electron microprobe determination of Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} in oxides and silicates and its application to petrologic problems. *Amer. Mineral.* **55,** 491–501

ANDERSEN, C. A. (1967) The quality of X-ray microanalysis in the ultrasoft X-ray region. *Brit. J. Appl. Phys.* **18,** 1033–1043.

BALLHAUSEN, C. J., AND H. B. GRAY (1964) *Molecular Orbital Theory.* Benjamin, New York.

BONELLE, C. (1966) Contribution à l'étude des metaux de transition du premier groupe, du cuivre et leur oxydes par spectroscopie X dans le domaine de 13 à 22 Å. *Ann. Phys.* **61,** 439–481.

BURNS, R. G. (1970) *Mineralogical Applications of Crystal Field Theory.* Cambridge Univ. Press Cambridge.

COTTON, F. A., AND G. WILKINSON (1966) *Advanced Inorganic Chemistry* John Wiley, New York.

DODD, C. G., AND G. L. GLEN (1968) Chemical bonding studies of silicates and oxides by X-ray emission spectroscopy. *J. Appl. Phys.* **39,** 5377–5384.

——— AND ——— (1969) A survey of chemical bonding in silicate minerals by X-ray emission spectroscopy. *Amer. Mineral.* **54,** 1299–1310.

FISCHER, D. W. (1965) Changes in soft X-ray *L* emission spectra with oxidation of first series transition metals. *J. App. Phys.* **36,** 2048–2053.

——— (1969) Vanadium $L_{II,III}$ X-ray emission and adsorption spectra from metal, oxides nitrides, carbides and borides. *J. Appl. Phys.* **40,** 4151–4163.

——— AND W. L. BAUN (1968) Band structure and the titanium $L_{II,III}$ X-ray emission and absorption spectra from pure metals, oxides, carbides and borides. *J. Appl. Phys.* **39,** 4757–4776

GLENN, G. L., AND C. G. DODD (1968) Use of molecular orbital theory to interpret X-ray *K*-absorption spectral data. *J. Appl. Phys.* **39,** 5372–5377.

GRAY, H. B. (1964) Molecular orbital theory for transition metal complexes. *J. Chem. Educ.* **4,** 2–10.

HEINRICH, K. F. J. (1967) The absorption correction model for microprobe analysis. *Trans. 2nd Nat. Conf. Electron Microprobe Analysis* Mass. Inst. Tech. Boston.

KELLY, T. K. (1966) Mass absorption coefficients and relevance in electron probe microanalysis. *Inst. Min. Metal.* **75,** 1359–1371

MITCHELL, K. A. R. (1969) The use of outer d-orbitals in bonding. *Chem. Rev.* **69**, 157–178.

PAULING, L. (1930) The structure of pseudobrookite. *Z. Kristallogr.* **73,** 97–112.

REED, S. J. B. (1965) Characteristic fluorescence corrections in electron-probe microanalysis. *Brit. J. Appl. Phys.* **16,** 913–926.

SMITH, D. G. W. (1965) The chemistry and mineralogy of some emery-like rocks from Sithean Slauigh, Strachur, Argyllshire. *Amer. Mineral.* **50**, 1982–2022.

——— AND R. K. O'NIONS (1971) Investigations of the Fe $L_{II,III}$ X-ray emission spectra of Fe by the electron microprobe. Part 1. Some aspects of the Fe $L_{II,III}$ spectra from metallic iron and hematite. *Brit. J. Appl. Phys.,* **4,** 147–159.

URCH, D. S. (1970) The origin and intensities of low energy satellite lines in X-ray emission spectra. *J. Phys. Chem.* **3,** 1275–1291.

Manuscript received, March 5, 1970; accepted for publication, March 12, 1971.