

## Low temperature preparation and characterization of intermetallics— $\text{Fe}_2\text{W}$ , $\text{FeMo}$ and some ternary $\text{Fe-W-Mo}$ systems

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**Abstract.** Monophase  $\text{Fe}_2\text{W}$  and  $\text{FeMo}$  intermetallics have been prepared by hydrogen reduction of  $\text{Fe}_2\text{WO}_6$  and  $\text{FeMoO}_4$  oxides respectively below 1050 K. The ternary intermetallics  $\text{Fe}_2\text{W}_{0.9}\text{Mo}_{0.1}$  and  $\text{FeMo}_{0.9}\text{W}_{0.1}$  have also been prepared by a similar method from the respective substituted oxides. The oxides and the intermetallics have been characterized by x-ray powder diffraction, x-ray photoelectron and Mössbauer spectroscopies. The observed negative isomer shift of Fe in the intermetallics is attributed to an increase in the electron density in Fe by electron transfer from W or Mo to Fe.

**Keywords.**  $\text{Fe}_2\text{W}$ ;  $\text{FeMo}$ ; low temperature preparation; photo-electron spectroscopy; Mössbauer spectroscopy.

### 1. Introduction

Low temperature preparation of alloys of refractory metals is of current interest both to save energy and for potential applications in catalysis due to the finely divided nature of the alloy (Cheetham 1980). Cheetham (1980) was the first to show the advantages of low temperature preparation of Mo-W alloys. Erdmann and Keller (1973) prepared actinide (lanthanide)-noble metal alloy phases by coupled hydrogen reduction. The method involved hydrogen reduction of metal oxides in the presence of the noble metals. Ferromolybdenum was prepared by hydrogen reduction from ferric molybdate (Pattnaik *et al* 1981). Here we report low temperature preparation of intermetallics  $\text{Fe}_2\text{W}$  and  $\text{FeMo}$  in pure monophase powder form by hydrogen reduction of the respective well characterized single phase oxides.

An intermetallic compound is a phase which crystallizes with a structure other than those of its components in the alloy system. Many of them are oxidation-resistant besides having high melting point and strength (Westbrook 1967). Generally, they are prepared by high temperature techniques such as arc melting. We considered it worthwhile to prepare refractory intermetallics  $\text{Fe}_2\text{W}$ ,  $\text{FeMo}$ ,  $\text{Fe}_2\text{W}_{0.9}\text{Mo}_{0.1}$  and  $\text{FeMo}_{0.9}\text{W}_{0.1}$  by hydrogen reduction of the well-characterized parent oxides having the required stoichiometry. We have employed x-ray powder diffraction, Mössbauer spectroscopy and x-ray photoelectron spectroscopy for characterization.

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## 2. Experimental

Pure  $\text{Fe}_2\text{O}_3$ ,  $\text{WO}_3$  and  $\text{MoO}_3$  were used for the preparation of  $\text{Fe}_2\text{WO}_6$  and  $\text{Fe}_2\text{WO}_{0.9}\text{Mo}_{0.1}\text{O}_6$  oxides. Stoichiometric ratios of the metal oxides were ground in an agate mortar with cyclohexane and then heated to 1070 K for 50 hours in an alumina boat. Intermediate grinding of the oxide mixture was done several times to ensure the formation of a homogeneous monophase product.

Pure iron powder, reduced initially in hydrogen, was used in addition to the above metal oxides for the preparation of  $\text{FeMoO}_4$  and  $\text{FeMo}_{0.9}\text{W}_{0.1}\text{O}_4$ . The well ground stoichiometric oxide mixture was pelletized and sealed in evacuated quartz tubes. The pellet was heated to 1070 K for 50 hours and then cooled to liquid nitrogen temperature to ensure the formation of the low temperature–low pressure  $\alpha$  phase of  $\text{FeMoO}_4$ .

The intermetallics were obtained by hydrogen reduction of these oxides at 1050 K. The reduction set-up consists of a horizontally placed externally heated translucent quartz tube. The observed decrease in weight due to reduction and the calculated weight losses were compared and used as the initial check to ensure complete reduction of the oxides before any other characterization was employed.

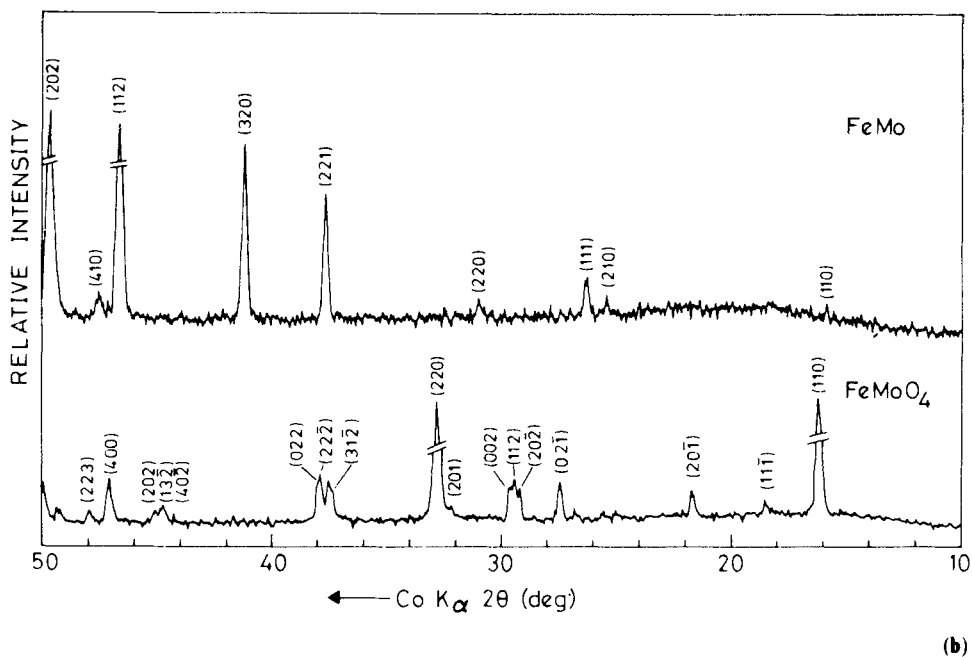
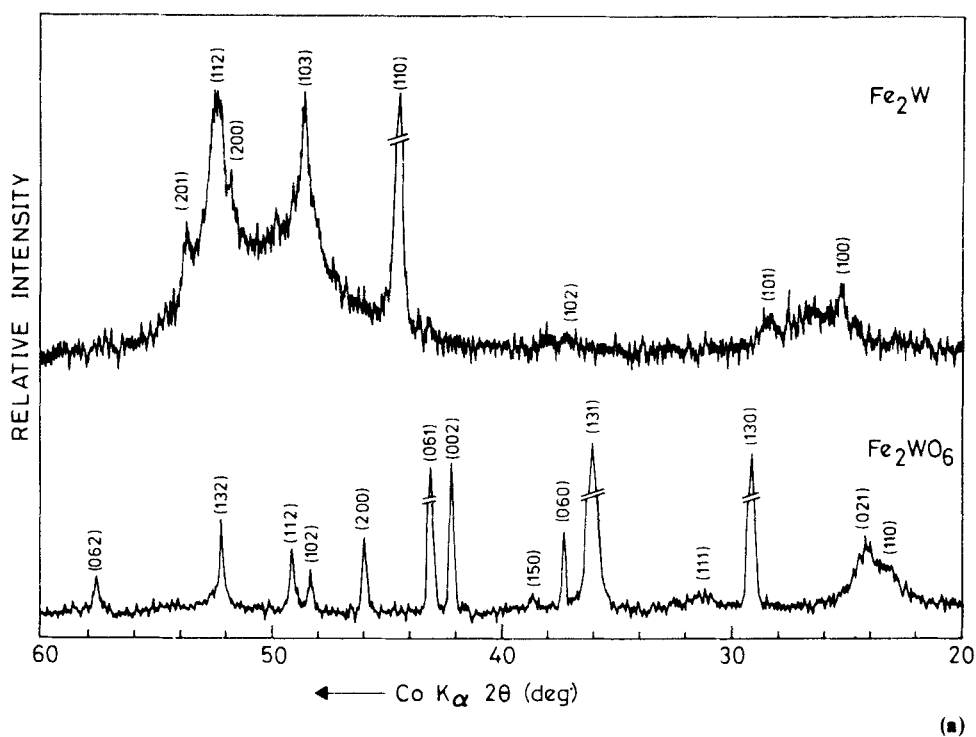
Room temperature x-ray powder diffractograms were recorded using a Philips x-ray diffractometer (PW 1050/70) with filtered  $\text{CoK}_\alpha$  radiation. The cell parameters calculated from the diffractograms were refined with a least squares programme CELN on the basis of the respective structures.

The xps studies were carried out in the ESCA 3-MARK II spectrometer of VG scientific (UK) with  $\text{AlK}_\alpha$  x-ray source. Binding energies reported here are with reference to  $\text{Au}(4f_{7/2})$  at  $83.7 \pm 0.2$  eV.

Mössbauer spectra were recorded at room temperature and the measurements were performed in the constant acceleration mode with a  $25 \text{ mC/Co}^{57}$  (Rh) source using an ECIL MBS 35 (India) Mössbauer spectrometer. All the samples show a single quadrupole split resonance. Mössbauer parameters—*isomer shift* and *quadrupole splitting*—were obtained by computer fitting of the spectra with Lorentzian lines and least square optimization.

## 3. Results and discussion

The x-ray diffractograms of  $\text{Fe}_2\text{WO}_6$  and  $\text{Fe}_2\text{W}$  are shown in figure 1(a).  $\text{Fe}_2\text{WO}_6$  has been reported to crystallize with columbite structure when prepared below 1070 K and with the  $\alpha\text{-PbO}_2$  structure when prepared above 1070 K (Leiva *et al* 1982). Difficulties were reported in obtaining the columbite variant of  $\text{Fe}_2\text{WO}_6$  as a single phase, since the  $\alpha\text{-PbO}_2$  variant also appeared to form at lower temperatures with small amounts of  $\alpha\text{-Fe}_2\text{O}_3$ .  $\text{Fe}_2\text{WO}_6$  prepared in this study was orthorhombic with cell parameters  $a = 4.591$  Å,  $b = 16.793$  Å and  $c = 4.97$  Å (space group *Pbcn*). The results are in good agreement with those previously reported by Leiva *et al* (1982). X-ray diffractograms of  $\text{FeMoO}_4$  and  $\text{FeMo}$  are shown in figure 1(b). Three polymorphs of  $\text{FeMoO}_4$  are known (1) low temperature–low pressure form of  $\alpha\text{-FeMoO}_4$ , (2) high temperature–low pressure form of  $\beta\text{-FeMoO}_4$  and (3) high pressure form of  $\text{FeMoO}_4\text{-II}$  (Sleight *et al* 1968). Pure single phase  $\alpha\text{-FeMoO}_4$  is obtained by either sufficient grinding at room temperature or by cooling to 78° K. In this study both these



**Figure 1.** X-ray powder diffractograms of (a)  $\text{Fe}_2\text{WO}_6$  and  $\text{Fe}_2\text{W}$ , and (b)  $\text{FeMoO}_4$  and  $\text{FeMo}$ .

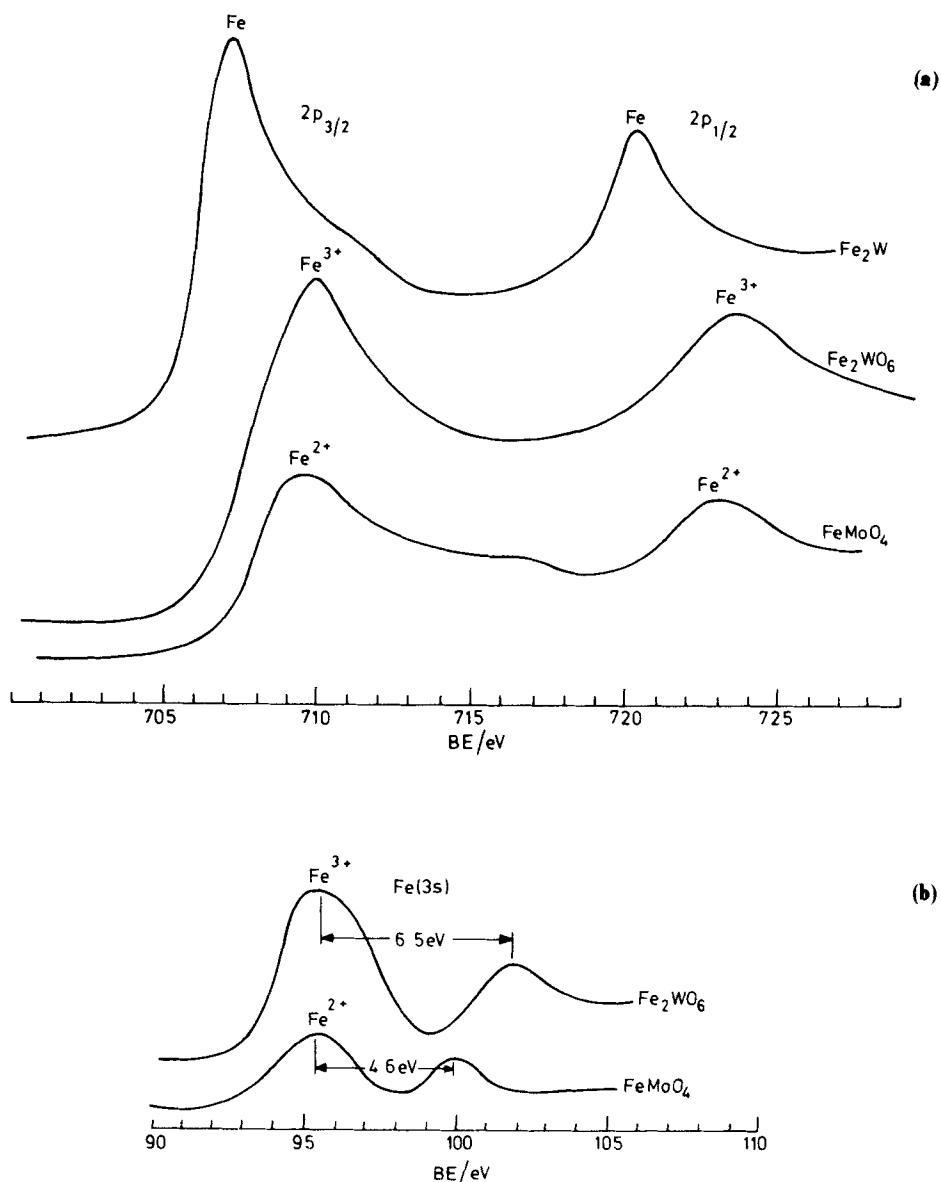
techniques were used to obtain  $\alpha$ -FeMoO<sub>4</sub> and the cell parameters are:  $a = 9.556$  Å,  $b = 8.745$  Å,  $c = 7.693$  Å and  $\beta = 113.62^\circ$ .

Fe<sub>2</sub>W belongs to the "Laves phases" class of intermetallic compounds. The Laves phases have compositions according to the formula  $AB_2$ , exemplified by the three prototype structures based on magnesium, viz. MgCu<sub>2</sub>, MgZn<sub>2</sub> and MgNi<sub>2</sub>. The  $A$  atoms are generally 22.5% larger than the  $B$  atoms so that they have an effective radius ratio of  $r_A/r_B = 1.225$ . The smaller  $B$  atoms are located at the corners of the tetrahedra and the  $A$  atoms are accommodated at the holes enclosed by the tetrahedra; the structure can be regarded as being made of two interpenetrating lattices of  $A$  and  $B$  atoms. While the three prototype structures have the same efficiency in space filling they differ in the stacking sequence of  $AB_2$  layers and hence in their unit over all dimensions. The MgCu<sub>2</sub> structure is cubic and the MgZn<sub>2</sub> and MgNi<sub>2</sub> structures are hexagonal. Fe<sub>2</sub>W belongs to the MgZn<sub>2</sub> type, wherein the tetrahedra formed by Fe atoms are joined alternatively base-to-base and point-to-point. Each W atom is also tetrahedrally coordinated to four other W atoms, but the arrangement is identical to the hexagonal Wurtzite structure. The Fe<sub>2</sub>W structure contains four formula units per cell and belongs to space group  $P6_3/mmc$ . The cell parameters of Fe<sub>2</sub>W prepared by the low temperature method are  $a = 4.743$  Å and  $c = 7.710$  Å.

FeMo is a sigma ( $\sigma$ ) phase intermetallic and this phase has received much detailed attention as its formation leads to embrittlement. Once they are nucleated, they grow to relatively large sizes and are particularly hard. The  $\sigma$  phase has a complex tetragonal structure with thirty atoms distributed on five special positions of space group  $P4_2/mnm$  in a unit cell with  $c/a \sim 0.51 - 0.54$  and  $c = 4.5 - 5.2$  Å. The  $\sigma$  phase is ordered and various atoms have a preference for one of the five positions. The cell parameters of FeMo prepared by us are:  $a = 9.190$  Å and  $c = 4.814$  Å. It should be noted that both the Laves phases and the sigma phase belong to a class that has been termed as tetrahedrally close-packed structures (t.c.p.) which involves packing of somewhat distorted atoms in distorted polyhedra. By adopting such arrangements, these structures achieve denser packing than could be obtained if geometrically close-packed structures were formed. Atomic coordination of 12, 14, 15 and 16 may occur and systematic classification of t.c.p. structures have been proposed based on the manner in which the corresponding coordination polyhedra interpenetrate. Cell parameters of both Fe<sub>2</sub>W and FeMo prepared by the hydrogen method, agree well with the reported values for the sample prepared by the conventional high temperature melting method.

Ionic radii of W<sup>6+</sup> and Mo<sup>6+</sup> are of the same value for the octahedral coordination (Shannon *et al* 1969). Hence substitution of Mo in Fe<sub>2</sub>WO<sub>6</sub> to give Fe<sub>2</sub>W<sub>0.9</sub>Mo<sub>0.1</sub>O<sub>6</sub> and W in FeMoO<sub>4</sub> to give FeMo<sub>0.9</sub>W<sub>0.1</sub>O<sub>4</sub> permits the basic structure to be retained. The corresponding intermetallics Fe<sub>2</sub>W<sub>0.9</sub>Mo<sub>0.1</sub> and FeMo<sub>0.9</sub>W<sub>0.1</sub> also retain the basic structure of Fe<sub>2</sub>W and FeMo respectively.

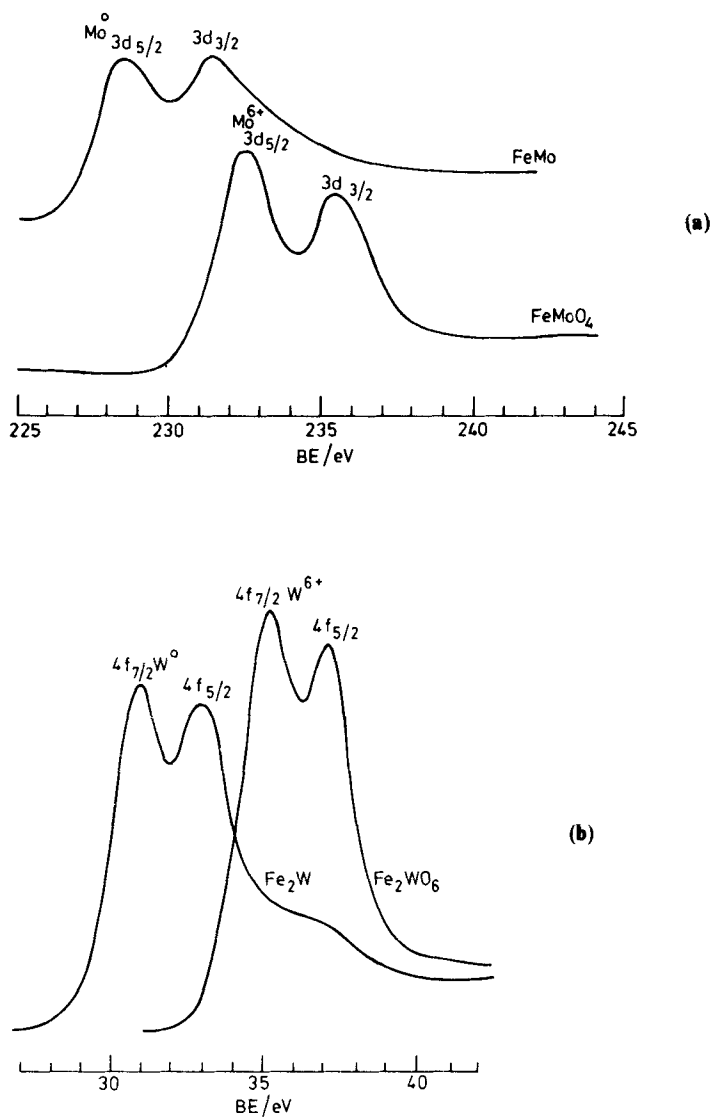
X-ray photoelectron spectra of Fe(2p) and Fe(3s) in Fe<sub>2</sub>WO<sub>6</sub> and FeMoO<sub>4</sub> are shown in figures 2a and b respectively. The shift of the 2p<sub>3/2</sub> peak to higher binding energy by 3.2 eV in Fe<sub>2</sub>WO<sub>6</sub> and to 2.5 eV in FeMoO<sub>4</sub> as compared to metallic iron shows the oxidation of Fe to be 3+ and 2+ states in these oxides respectively (Vasudevan *et al* 1979). Further, the exchange splitting of Fe(3s) with a value of 6.5 eV and 4.6 eV respectively in Fe<sub>2</sub>WO<sub>6</sub> and FeMoO<sub>4</sub> indicate the high spin configuration of Fe in these oxides (Rao *et al* 1979). The 3d photoelectron spectrum of Mo in FeMoO<sub>4</sub> and FeMo are shown in figure 3(a). The 4 eV shift of Mo(3d<sub>5/2</sub>) in FeMoO<sub>4</sub> shows the oxidation state of Mo to be 6+ (Haber *et al* 1976). The W(4f) spectrum in



**Figure 2.** (a) Fe (2p) core level photoelectron spectra in FeMoO<sub>4</sub>, Fe<sub>2</sub>WO<sub>6</sub> and Fe<sub>2</sub>W, (b) Fe (3s) core level splitting in FeMoO<sub>4</sub> and Fe<sub>2</sub>WO<sub>6</sub>.

Fe<sub>2</sub>WO<sub>6</sub> and Fe<sub>2</sub>W are shown in figure 3(b). The oxidation state of W is found to be 6+ in Fe<sub>2</sub>WO<sub>6</sub> as expected (Haber *et al* 1976). The Fe (2p) lines of the intermetallics indicate Fe to be in metallic form. Further the 4f line of W in Fe<sub>2</sub>W and the 3d<sub>5/2</sub> line of Mo in FeMo also indicate the metallic nature in these intermetallics respectively. Binding energies of core levels in the oxides and the corresponding intermetallics are given in table 1a.

Mössbauer spectra of the oxides and the corresponding intermetallics are shown in



**Figure 3.** (a) Mo (3d) core level photoelectron spectra in FeMoO<sub>4</sub> and FeMo, (b) W (4f) photoelectron spectra in Fe<sub>2</sub>W and Fe<sub>2</sub>WO<sub>6</sub>.

figures 4a, b respectively. All the samples show a single quadrupole split resonance. The value of the isomer shift  $\delta$  and of the quadrupole splitting ' $\Delta E_q$ ' of both the oxides and the intermetallics are shown in table 1b. The position of the oxides in the scatter plot based on  $\Delta E_q$  and  $\delta$  clearly confirms the oxidation state of Fe as 3+ in Fe<sub>2</sub>WO<sub>6</sub> and as 2+ in FeMoO<sub>4</sub> respectively, both being in the high spin configuration (Brady *et al* 1965). xps results thus support the Mössbauer results. It should be noted that Mössbauer studies on Fe<sub>2</sub>WO<sub>6</sub> have been reported for the first time. Fe<sub>2</sub>WO<sub>6</sub> consists of hexagonal close packed planes of O<sup>2-</sup> anions in which only half the octahedral sites are occupied by the metal atoms, Fe or W and the resulting octahedra

**Table 1(a).** Core-level binding energies of the oxides and the intermetallics

Sample	Fe(2p <sub>3/2</sub> ) B.E. (eV)	Fe(3s) Splitting (eV)	Mo(3d <sub>5/2</sub> ) B.E. (eV)	W(4f <sub>7/2</sub> ) B.E. (eV)	O(1s) B.E. (eV)
Fe <sub>2</sub> WO <sub>6</sub>	710.0	6.5	—	35.3	530.1
Fe <sub>2</sub> W	706.5	—	—	31.0	—
FeMoO <sub>4</sub>	709.2	4.6	232.5	—	530.8
FeMo	707.9	—	228.2	—	—

B.E. = binding energy

**Table 1(b).** Mössbauer parameters of the oxides and the intermetallics

Sample	Isomer shift* mm/sec ± 0.02	Quadrupole splitting mm/sec ± 0.02
Fe <sub>2</sub> WO <sub>6</sub>	0.32	0.79
Fe <sub>2</sub> W <sub>0.9</sub> Mo <sub>0.1</sub> O <sub>6</sub>	0.38	0.84
FeMoO <sub>4</sub>	1.10	1.50
FeMo <sub>0.9</sub> W <sub>0.1</sub> O <sub>4</sub>	1.12	1.53
Fe <sub>2</sub> W	-0.25	0.21
Fe <sub>2</sub> W <sub>0.9</sub> Mo <sub>0.1</sub>	-0.35	0.24
FeMo	-0.24	0.16
FeMo <sub>0.9</sub> W <sub>0.1</sub>	-0.24	0.21

\* Isomer shift values are relative to Fe metal.

share a pair of screw edges in such a way that zigzag chains are formed parallel to the C direction (Leiva *et al* 1982). Thus in Fe<sub>2</sub>WO<sub>6</sub> all the Fe ions are crystallographically equivalent. Hence the double resonance observed is not due to either iron at two different sites nor due to iron in two different oxidation states but is a single quadrupole resonance. The small values of the quadrupole splitting further supports the argument since Fe<sup>3+</sup> ion possesses a spherical symmetry charge distribution and does not give rise to interaction with the electrical quadrupole moment. The splitting is thus caused solely by the field gradients produced by the crystal lattice around the Fe nucleus.

Mössbauer studies of FeMoO<sub>4</sub> have been reported by Sleight *et al* (1968) and our results are in agreement with these values. Increase in the electron density and in field gradient at the Fe nucleus, on substitution of Mo in Fe<sub>2</sub>WO<sub>6</sub> and W in FeMoO<sub>4</sub> respectively, is indicated from the increase in the isomer shift and quadrupole splitting values.

Fe<sub>2</sub>W Mössbauer studies were reported by Nevitt *et al* (1964) and our values agree with the reported value. To the best of our knowledge, FeMo Mössbauer studies have not been reported in the literature. The negative value of the isomer shift in the case of intermetallics indicates a charge transfer to Fe from W or Mo. Sham *et al* (1979) reported such charge transfer in their studies on Au alloys and intermetallics using xps and Mössbauer spectroscopy.

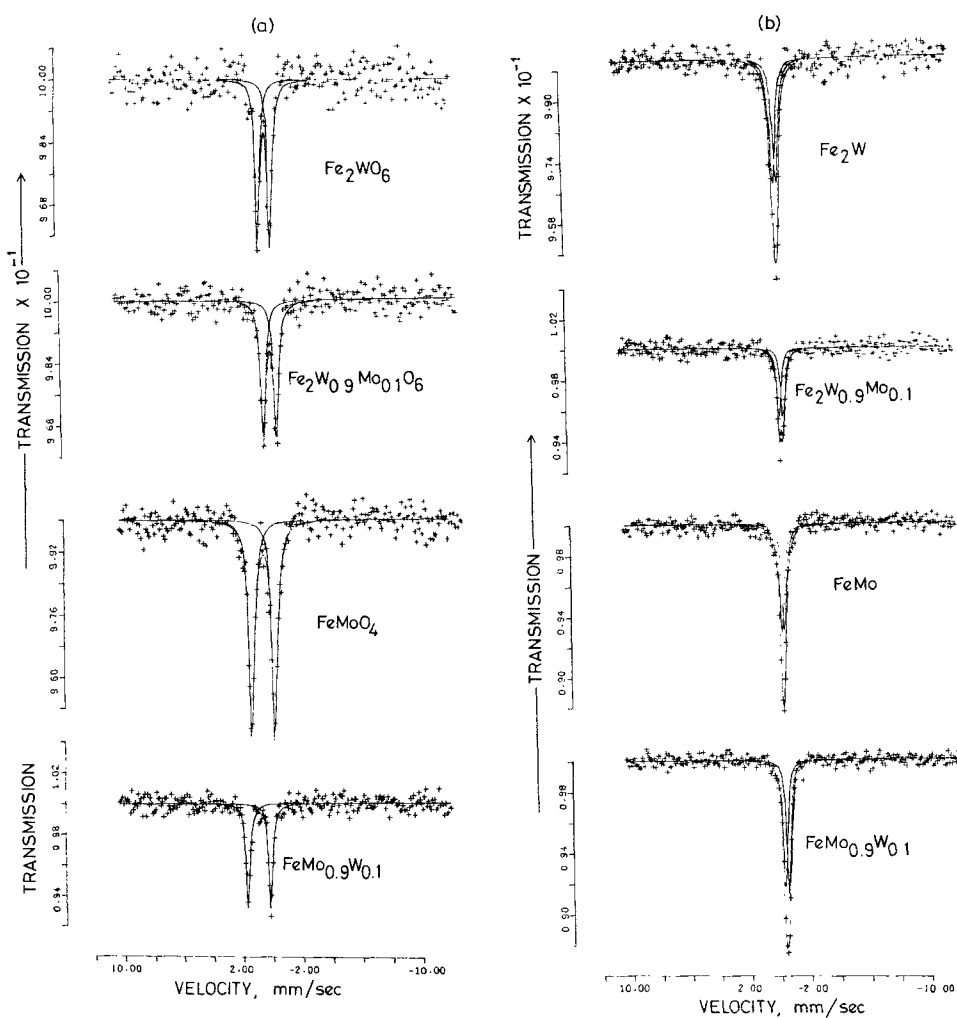


Figure 4. Fe Mössbauer spectra of (a) the oxides, and (b) the corresponding intermetallics.

In conclusion,  $\text{Fe}_2\text{W}$ ,  $\text{FeMo}$  and substituted intermetallics have been prepared by hydrogen reduction of  $\text{Fe}_2\text{WO}_6$ ,  $\text{FeMoO}_4$  and the respective substituted oxides. Electronic structures of both the oxides and the intermetallics have been characterised by XPS and Mössbauer spectroscopy.

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