

^{57}Fe Mössbauer and Mo K-EXAFS Investigations of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$, an Interesting Mixed-Valent Oxide System

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Ferrites of the formula $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$, prepared by a soft-chemistry route, show mixed valence states of both iron and molybdenum cations. Mössbauer studies show that Fe^{2+} and Fe^{3+} ions are present on both the A and B sites, giving Fe an average oxidation state between 2+ and 3+. Molybdenum is present in the 3+ and the 4+ states on the B sites. The presence of Mo in the 3+ state has been established by determining the $\text{Mo}^{3+}-\text{O}$ distance (2.2 Å), for the first time, by Mo K-EXAFS. The mixed valence of Fe on both the A and B sites and of Mo on the B sites is responsible for the fast electron transfer between the cations. All the Mössbauer parameters including the line width show a marked change at a composition ($x \approx 0.3$) above which the concentration of Fe_A^{2+} increases rapidly.

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Introduction

MoFe_2O_4 is an interesting inverse spinel derived from magnetite, Fe_3O_4 , where both Fe and Mo can occur in more than one oxidation state and Fe is present in two distinct sites, A and B. Abe *et al.* (1, 2) first suggested the cation distribution of MoFe_2O_4 to be $\text{Fe}^{2+}[\text{Mo}^{4+}\text{Fe}^{2+}]\text{O}_4$, but later proposed (3) that it was also necessary to consider the distribution $\text{Fe}^{3+}[\text{Mo}^{3+}\text{Fe}^{2+}]\text{O}_4$. Based on neutron diffraction, Mössbauer and mag-

netic measurements, Ghose *et al.* (4) concluded the formal valence distribution to be $\text{Fe}^{2+}[\text{Mo}^{4+}\text{Fe}^{2+}]\text{O}_4$. Mössbauer studies by Gupta *et al.* (5), however, indicated the distribution to be $\text{Fe}_{0.5}^{3+}\text{Fe}_{0.5}^{2+}[\text{Mo}^{3+}\text{Fe}_{0.5}^{2+}\text{Fe}_{0.5}^{3+}]\text{O}_4$; this distribution was considered satisfactory to explain fast electron transfer on A-site iron. Ramdani *et al.* (6) have more recently investigated MoFe_2O_4 and proposed complex cation equilibria involving Fe_B^{2+} , Fe_A^{3+} , Fe_B^{3+} , Fe_A^{2+} , Mo^{3+} , and Mo^{4+} ions. They show that Fe has an average valence near 2.5+ with fast electron transfer ($\tau < 10^{-8}$ sec) on both tetrahedral and octahedral sites and that Mo could have a small

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occupancy of the A sites at high temperatures. The Fermi energy probably lies below the mobility edge in the $\text{Mo}^{4+(3+)}$ band; some localized spins may also be associated with the Mo array. Ramdani (7) has also suggested that $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ is best represented by $[\text{Fe}_{1-\beta}^{3+}\text{Fe}_{\beta}^{2+}]_A[\text{Mo}_{x-\alpha}^{3+}\text{Mo}_{\alpha}^{4+}\text{Fe}_{1+\alpha-\beta}^{2+}\text{Fe}_{1-x-\alpha+\beta}^{3+}]_B\text{O}_4$, where β is close to $x/2$ and α increases with x but remains small when $0 < x < 1.0$. Bouet *et al.* (8) also support this formulation based on thermogravimetry and calorimetry. This is in contrast to the conclusions of Furukawa (9) who proposed that only Mo^{4+} is in the octahedral sites of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$. Domenichini *et al.* (10) have further modified the distribution proposed by Bouet *et al.* (8) based on thermal analysis and infrared spectroscopy. Clearly, the nature of metal oxidation states and site occupancies in $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ are far from being clear. For this purpose, we have prepared $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ ($0.2 \leq x < 0.6$) compositions by a low-temperature soft-chemistry route and investigated them by ^{57}Fe Mössbauer spectroscopy and extended X-ray absorption fine structure (EXAFS) analysis. The ferrites prepared by us were in fine particulate form and could be readily oxidized. We have also investigated the oxidized forms of these spinels. The present study clearly establishes the presence of both Fe and Mo in mixed-valent states on the B-sites and shows that the proportion of Fe^{2+} on the A site increases markedly with Mo content.

Experimental

Precursors of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ were prepared as an oxide mixture by precipitation of Fe^{2+} , Fe^{3+} , and Mo^{5+} chloride solutions in an alkaline medium. The ferrites were then obtained by thermal treatment first in air and then in H_2 - N_2 mixtures between 673 and 973 K. The spinel phases were fine-grained with a crystallite size close to 50 nm. The spinels so prepared were heated in air at different temperatures in order to study the

changes brought about by oxidation. X-ray diffraction patterns of the $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ samples showed them to be monophasic without any $\text{Fe}_2\text{Mo}_3\text{O}_8$ impurity.

^{57}Fe Mössbauer spectra were recorded at room temperature with a constant acceleration spectrometer using a 25-mCi ^{57}Co source in Pd matrix (Amersham Corporation, U.K.). Absolute velocity calibration was performed with an Fe foil of 25- μm thickness and the isomer shifts are reported with respect to the absorber. A nonlinear least-squares curve fitting procedure was used to achieve the best fit to the experimental data. The spectra were computer fitted using a general Lorentzian routine on a VAX 88 system. Most of the curves could be fitted as two symmetric six-line patterns with intensity ratios of 3 : 2 : 1.

EXAFS spectra were recorded using a Rigaku spectrometer with a rotating anode X-ray generator (Ru-200B, Rigaku, Japan). A Ge(220) crystal was used as the monochromator with a 0.1-mm slit for X-rays from a Cu target. The spectral resolution was about 8 eV at 20 keV incident energy. The oxide samples were pressed into self-supporting wafers after mixing with polyethylene powder (Merck). The thickness of the wafer was adjusted so that the edge jump ($\mu\text{.d}$) in the EXAFS was 1.5 in every case. X-ray absorption data were collected preedge in steps of 5 eV for 100 eV and after the edge in steps of 1 eV up to 700 eV. EXAFS spectra of the reference compound, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, were recorded under similar conditions. Fourier transforms (FT) of the EXAFS data were obtained with $k_{\text{min}} \sim 3.75$ and $k_{\text{max}} \sim 12.75 \text{ \AA}^{-1}$ after weighting the data by k^3 .

Results and Discussion

Mössbauer studies of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$. Figure 1 shows the ^{57}Fe Mössbauer spectra of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ compositions with $x = 0.2, 0.29, 0.53, \text{ and } 0.58$. With increasing x , there

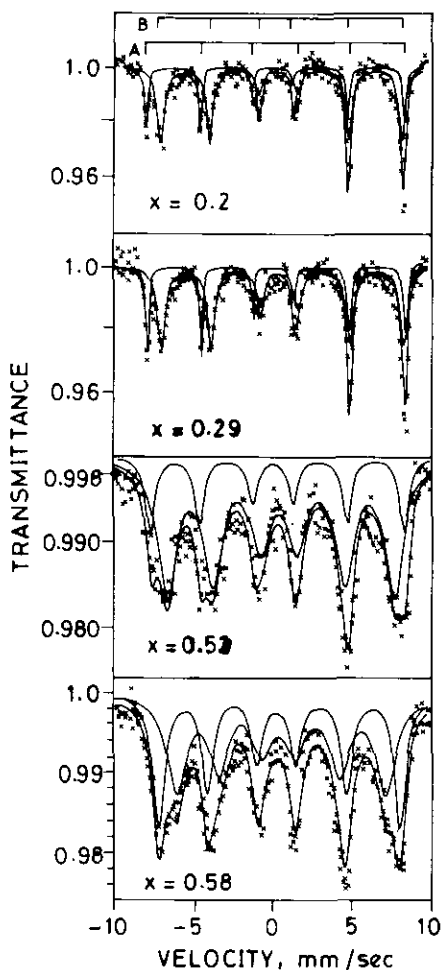


FIG. 1. Mössbauer spectra of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ at room temperature.

is increased broadening as was noted by earlier authors (3, 5, 6). Contrary to the report of Furukawa (9), we have been able to fit the spectra into two six-finger patterns corresponding to the A (tetrahedral) and the B (octahedral) sites. We had to include a third six-finger pattern only in samples that were found to contain a $\text{Fe}_2\text{Mo}_3\text{O}_8$ impurity by X-ray diffraction. Such compositions result from the decomposition of the spinels at medium temperatures in the ceramic route or from a highly reducing atmosphere in our

preparation based on the soft-chemistry route. In order to ensure that the third six-finger pattern was due to a $\text{Fe}_2\text{Mo}_3\text{O}_8$ impurity, we prepared an impure spinel ferrite containing this phase. We show the Mössbauer spectra of such samples on Fig. 2. We therefore conclude that the Mössbauer spectra of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ can be satisfactorily described by one six-finger pattern each for the A and B sites, confirming that Fe has an average oxidation state of $\sim +2.5$ on both sites (6) at room temperature.

In Table I we present the results of our Mössbauer studies of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ compositions. In Figs. 3 and 4, we show the variation of the magnetic hyperfine field and the isomer shift, respectively, with the molybdenum content for both the A and the B sites. In Fig. 5 we show the variation of the peak broadening with composition. In Table I we have listed the ratios of intensities (areas under the peaks) due to the B and A sites. The B/A ratio, which is ideally 2 in Fe_3O_4 , becomes much higher in $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ for small x (≤ 0.53), but decreases sharply when $x = 0.58$.

We see from Fig. 3 that the hyperfine field decreases with x for both the A and B sites, but the variation is greater for the B site. The decrease in the hyperfine field of the A site with increasing x arises from the substi-

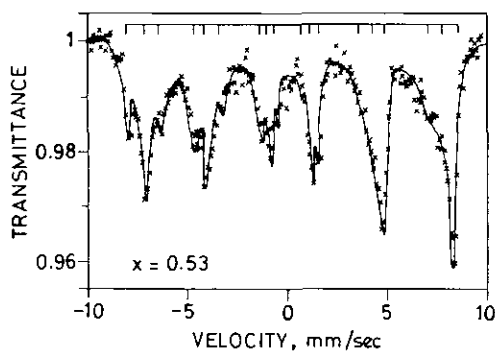


FIG. 2. Mössbauer spectra of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.53$) with $\text{Fe}_2\text{Mo}_3\text{O}_8$ impurity.

TABLE I
MÖSSBAUER RESULTS ON $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$

Composition	Isomer shift (mm/sec) ^a ± 0.03	Internal magnetic field (kOe)	Quadrupole splitting (mm/sec) ± 0.03	Half-width (mm/sec)
$x = 0.2$	A 0.31	494	0.04	0.26
	B 0.67 (2.9)	465	0.05	0.58
$x = 0.29$	A 0.33	494	0.05	0.29
	B 0.66 (2.3)	463	0.08	0.63
$x = 0.53$	A 0.45	472	0.04	0.76
	B 0.59 (2.4)	419	0.12	1.48
$x = 0.58$	A 0.50	464	0.05	0.91
	B 0.57 (1.2)	402	0.14	1.51

^a B/A intensity ratio is shown in parantheses; uncertainty in the ratio is ± 0.3.

tution of Fe^{3+} ions (with d^5 configuration) by Fe^{2+} ions (d^6) possessing a lower moment. The decrease is nonlinear and becomes prominent when $x \approx 0.3$, implying that the proportion of Fe^{2+} on the A sites also varies nonlinearly with x . It is also possible that at high x , molybdenum partly occupies A sites. The significant decrease in the hyperfine field of the B site can arise from the substitution of iron by molybdenum. The decrease becomes marked at $x = 0.3$ in the case of the B site as well.

From Fig. 4 we see that the isomer shift of the A site increases progressively, but nonlinearly, with increasing x . This confirms that the formal oxidation state of Fe in the A sites decreases with increasing the molybdenum content. The decreasing isomer shift of Fe in the B sites with increasing x could imply that the oxidation state of Fe increases, but is more likely to be due to the dilution effect caused by the presence of molybdenum. Kündig *et al.* (11) have indeed

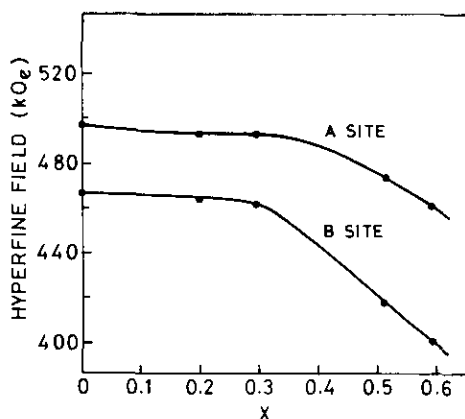


FIG. 3. Variation of hyperfine field of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ with Mo content on A and B sites. Lines have been drawn to guide the eye.

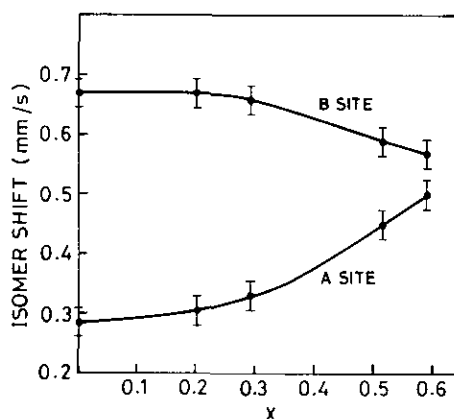


FIG. 4. Variation of the Fe isomer shifts with Mo content on A and B sites. Lines have been drawn to guide the eye.

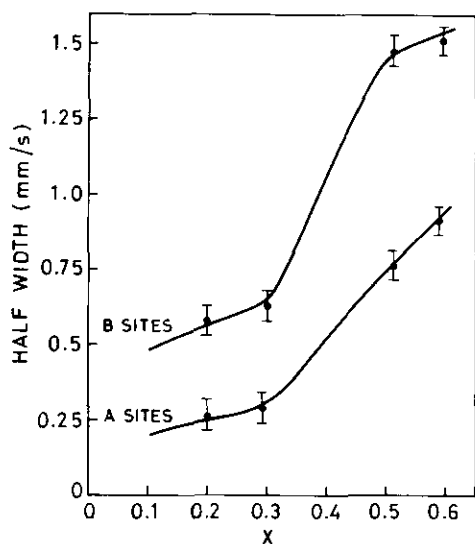


FIG. 5. Variation of the half-width of the Mössbauer spectra with Mo content.

shown that such dilution effects decrease the isomer shift. It is interesting that the variation in the isomer shifts on both the A and the B sites becomes significant when $x > 0.3$.

Figure 5 shows that the Mössbauer peak broadening increases with the molybdenum content for both the A and B sites. We also observe a small increase in the quadrupole splitting (Table I) on the B sites in samples with high molybdenum content. Since the different compositions had the same crystallite size (400–600 Å), the peak broadening is likely to be related to the valence distribution of Fe and Mo which promotes fast electronic transfer at high Mo content. Accordingly, oxidized $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ with mainly Fe^{3+} and Mo^{6+} show sharper spectra. The line broadening increases markedly at $x = 0.3$ just like the other Mössbauer parameters, suggesting a common origin. Since the peak broadening is more prominent for the B sites than for the A sites, it would appear that molybdenum goes preferentially to the B sites, as expected.

Mössbauer studies of oxidized $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$. Finely grained samples of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ are very reactive with respect to oxygen. We can, therefore, oxidize the cations in these samples at low temperatures to defect spinel ferrites (8). We have examined the oxidation of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ with low ($x = 0.2$) and high ($x = 0.58$) molybdenum contents. In Fig. 6, we compare the Mössbauer spectra of the samples subjected to oxidation at different temperatures with those of the original ferrites. We see that at 423 K, no important change occurs in both compositions and the spectra can still be fitted into two six-finger patterns. This observation implies that up to 423 K the valence state of iron is stable. The relatively high oxidation temperature is likely to be due to the fact that the fine particulates of the ferrites become slightly oxidized on the surface even at room temperature. Such an oxidized layer makes it difficult for oxygen to diffuse up to 423 K.

The spectrum of the $x = 0.2$ sample oxidized at 513 K could be fitted into a single six-finger pattern, suggesting that the valence states of iron are the same in both the A and the B sites; i.e., Fe^{2+} ions are oxidized completely at 513 K. The presence of only Fe^{3+} does not permit a distinction between A and B sites. In contrast, in the case of the $x = 0.58$ sample, the spectrum could be fitted to two six-finger patterns up to 573 K, showing that, in this composition, the Fe^{2+} ions are more stable to oxidation, part of the Fe^{2+} ions still being present at 573 K. It is necessary to carry out the oxidation at 648 K in order to attain complete oxidation of the Fe^{2+} ions in this composition. The relative stability of high molybdenum content ferrites to oxidation is not surprising if we consider the proportion of the Fe^{2+} ions present on the A sites. It has been demonstrated elsewhere that Fe^{2+} is more stable in a tetrahedral rather than in an octahedral environment (12). With increasing Mo content Fe^{2+} ions are stabilized, be-

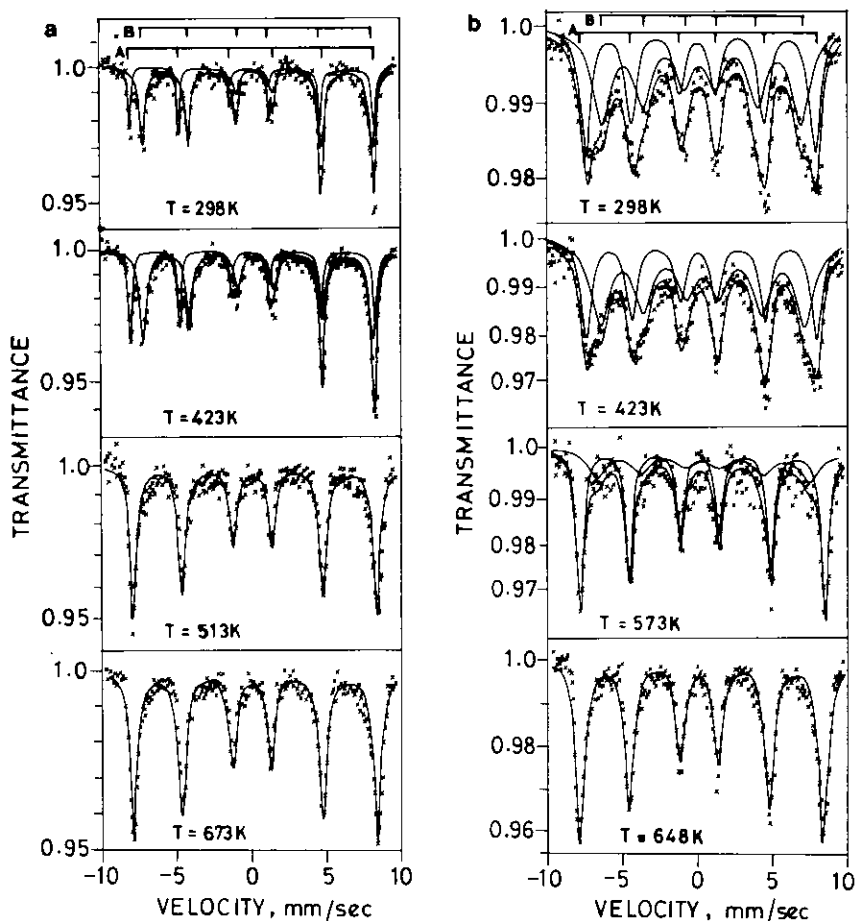


FIG. 6. Changes in the Mössbauer spectra of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ on oxidation at different temperatures: (a) $x = 0.2$ and (b) $x = 0.58$.

cause the proportion of Fe^{2+} ions on the A sites increases.

Mo K-EXAFS studies of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$. As mentioned earlier, MoFe_2O_4 has been suspected to contain part of the Mo as octahedral Mo^{3+} ions (5, 6). The itinerant electron properties as well as some of the localized magnetic properties of this ferrite have been interpreted by assuming the presence of a Mo band containing Mo in the 3+ and 4+ states. Our Mössbauer results of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ have provided direct information on the Fe states on both the A and the B sites and only indirect information on the

Mo states in the ferrites. In order to probe the nature of Mo, we have carried out the Mo K-EXAFS of two compositions ($x = 0.29$ and 0.58).

In Fig. 7, we show the Fourier transforms of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.29$ and 0.58) along with those of the reference compound, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$. The FT of the $x = 0.58$ composition has three peaks, at 1.52, 1.96, and 2.52 Å. The first peak occurs at the same value of r as that in the reference compound and probably arises from $\text{Mo}^{6+}-\text{O}$ coordination resulting from the surface oxidation of the ferrite (shown by an asterisk). The peak

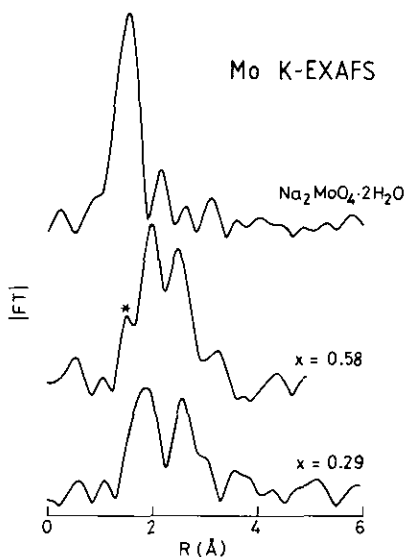


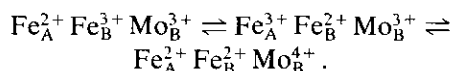
FIG. 7. Fourier transform of the Mo K-EXAFS of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ for $x = 0.29$ and $x = 0.58$. Asterisk corresponds to $\text{Mo}^{6+}\text{-O}$ coordination.

at 1.96 \AA would be expected to comprise coordinations involving Mo in the lower oxidation states. The peak at 2.52 \AA , however, arises due to metal-metal coordination. The FT of the $x = 0.29$ composition, on the other hand, shows one broad feature at 1.9 \AA due to oxygen coordination. Curve-fitting analysis was carried out on the inverse-transformed data using the phase and amplitude parameters from $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$. The best fit was obtained when three sets of Mo-O parameters were employed. The results of the curve-fitting analysis are listed in Table II. Curve-fitting analysis (Fig. 8) gives two important features at 2.0 and 2.2 \AA in both compositions. A Mo-O distance of 2.0 \AA is found in MoO_2 (Mo in the $4+$ state) and can be assigned to $\text{Mo}^{4+}\text{-O}$ coordination in the ferrites. The observation of a Mo-O distance of 2.2 \AA is unique. We ascribe this distance to a $\text{Mo}^{3+}\text{-O}$ octahedral coordination. The high value of the effective coordination number found in the EXAFS analysis for this phase rules out the possibility of the

occurrence of such a large Mo-O distance arising from a distorted coordination polyhedron involving Mo species of a higher oxidation state. Thus, the present EXAFS results provide direct evidence for the presence of a significant proportion of Mo^{3+} species in these ferrites. Furthermore, the relative proportion of Mo^{3+} and Mo^{4+} appears to be constant in $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$, as judged by the EXAFS data.

Conclusions

The present study of $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ clearly establishes that molybdenum is in a mixed valence state, being present in both the $3+$ and $4+$ states. We have thus, for the first time, been able to obtain a measure of the $\text{Mo}^{3+}\text{-O}$ distance by means of Mo K-EXAFS measurements. Based on our Mössbauer studies, we conclude that most of the molybdenum preferentially goes to the B sites and accordingly favors Fe^{2+} on the A sites. The broadening of the Mössbauer peaks may be due to the fast electron transfer between $\text{Mo}^{3+}/\text{Mo}^{4+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions; the broadening of the features (due to both A and B sites) becomes marked when the Mo content is fairly high, $x > 0.3$, at which composition the proportion of Fe^{2+} ions on the A sites increases. Fast electron transfer in $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ is due to the mixed valence of both the Fe and Mo on the A and the B sites. The main equilibria in these ferrites are

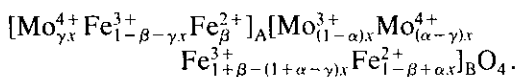


It is possible that we have to consider the presence of a small proportion of Mo^{4+} on the A sites as well. This would involve a term such as $\text{Fe}_A^{2+} \text{Fe}_B^{2+} \text{Mo}_A^{4+}$. We feel that we can by and large understand the cationic distribution of these ferrites by making use of the expression recently suggested by Domenichini *et al.* (10):

TABLE II
Mo K-EXAFS RESULTS ON Mo_xFe_{3-x}O₄

System		N	R(Å)	Δσ ² (Å ²)
Na ₂ MoO ₄ · 2H ₂ O (ref.)		4	1.77	—
Mo = 0.58 ^a	Mo ⁴⁺	1.0	1.97	0.0005
	Mo ³⁺	5.0	2.24	0.0005
Mo = 0.29 ^a	Mo ⁴⁺	1.0	1.98	0.002
	Mo ³⁺	4.3	2.22	0.001

^a There is a feature at 1.8 Å due to Mo⁶⁺-O distance arising from surface oxidation of the ferrite. The proportion of this species is higher in the x = 0.58 composition.



In Fig. 9, we show how the coefficients α, β, and γ vary with the molybdenum content, according to Domenichini *et al.* The Mo³⁺/Mo⁴⁺ ratio is constant and not dependent on x. Our EXAFS results seem to be consistent with this observation. The β coefficient of Fe²⁺ on the A sites however increases sharply above x = 0.3, in agreement with our Mössbauer results. The γ coefficient (Mo on A sites) is close to zero, since Mo would prefer to be on the B sites. The variation of the B/A intensity ratio in Table I can be understood in terms of Fig. 9. The ratio is larger than 2 at small x essentially because the Fe²⁺/Fe³⁺ ratio in the B site is greater than unity (this ratio is unity in Fe₃O₄). At high x, Fe_A²⁺ increases and Mo also goes into

B sites, thereby affecting the B/A ratio adversely.

A comment on the itinerancy of the electrons in Mo_xFe_{3-x}O₄ would be in order. Fe₃O₄ is a degenerate material and shows a resistivity increase due to the Verwey transition at 150 K (T_v). Mo_xFe_{3-x}O₄ samples show degenerate behavior with very low resistivity and at some temperature T₁, depending on the value of x, show an increase in resistivity. The value of T₁ decreases with increasing x and has a value of 120 K when x = 0.53. This observation suggests greater itinerancy of electrons with the incorporation of Mo in Fe₃O₄.

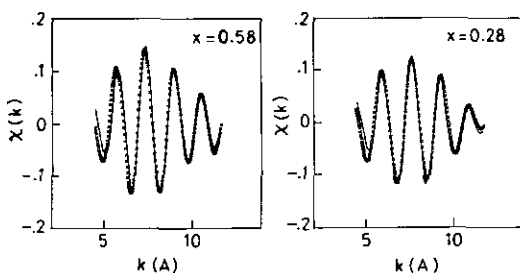


FIG. 8. Inverse transforms of Mo_xFe_{3-x}O₄ for x = 0.29 and x = 0.58.

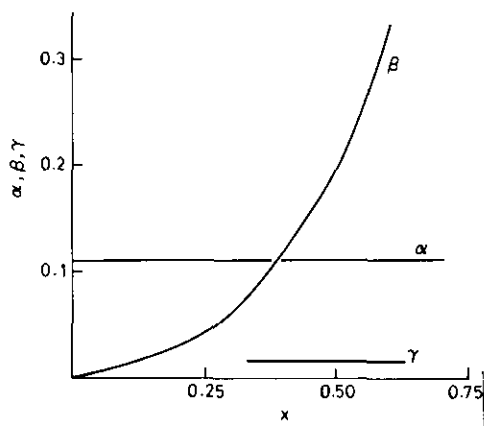


FIG. 9. Variation of the coefficients α, β, and γ with the molybdenum content.

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