

An ^{57}Fe Mössbauer Effect Study of Magnetic Ordering in the Fe_2O_3 - Cr_2O_3 System

T. BIRCHALL

Chemistry Department, McMaster University, Hamilton, Ontario, Canada

AND

A. F. REID

Division of Mineral Chemistry, CSIRO, Box 124, Port Melbourne, Australia

Received May 6, 1974

^{57}Fe Mössbauer effect spectra have been obtained as a function of temperature for a series of Fe_2O_3 - Cr_2O_3 compositions in the range 0.2-75% Fe_2O_3 . From 30% of Fe_2O_3 upwards, the dependence of the reduced internal magnetic field $H_{\text{eff}}(T)/H_{\text{eff}}(T=0)$ on reduced temperature, T/T_N , was found to be identical with that for α - Fe_2O_3 , indicating the persistence of Fe_2O_3 -type ordering over this composition range. For 0.2% of $^{57}\text{Fe}_2\text{O}_3$ in Cr_2O_3 , the reduced field values fall far below those for α - Fe_2O_3 or Cr_2O_3 , and weak coupling of Fe_3^+ with Cr^{3+} has been inferred.

A Morin transition similar to that for α - Fe_2O_3 was not present for samples containing 75% of Fe_2O_3 . Quadrupole shifts ϵ were found to be negative and diminishing between 75 and 30% Fe_2O_3 , and positive between 20 and 0.2%. The limiting value at lowest dilution of 0.113 ± 0.010 mm/sec corresponds to a nuclear quadrupole coupling constant e^2qQ of 0.45 ± 0.04 , approximately half that for α - Fe_2O_3 . Cone angles for Fe^{3+} spin vectors in the spin-spiral arrangements for intermediate compositions have been derived, and are similar to, but less extreme than those deduced from neutron diffraction data.

Introduction

Although both α - Fe_2O_3 and Cr_2O_3 exhibit the rhombohedral corundum-type crystal structure (1) and form a continuous solid solution series (2), it has been established by neutron diffraction studies that their magnetic structures are quite different (3, 4). For α - Fe_2O_3 at 298°K, the spins within any rhombohedral (111) plane, i.e., hexagonal (003) plane, are parallel, with adjacent planes coupled antiferromagnetically. Lowering the temperature results in a change in spin direction from within the (111) plane to a sequence $++--$ along the [111] axis, i.e., hexagonal c axis. This occurs at approximately 260°K (3, 5-8). In Cr_2O_3 , the spins were found to be directed along the [111] axis in

the sequence $+ - + -$, antiparallel within the (111) planes (4, 9).

The magnetic exchange constants for the various nearest-neighbour pairs in Fe_2O_3 and in Cr_2O_3 have been derived from inelastic neutron scattering data by Samuelson and co-workers (6, 10), and they have also shown that for α - Fe_2O_3 , the internal magnetic field at the Fe nucleus, H_{eff} , as determined by Mössbauer effect (5) shows the same temperature dependence as the sublattice magnetization.

In a magnetic and neutron diffraction study of the Fe_2O_3 - Cr_2O_3 system, Cox, Takei, and Shirane (11) showed that the magnetic phenomena observed could be interpreted in terms of spiral spin configurations. Addition of Fe_2O_3 to Cr_2O_3 creates a cone spiral with

both the cone axis and the spiral wave vector lying initially along the [111] axis. At an intermediate composition, a transition in spin-ordering occurs, and a new cone axis is produced perpendicular to the [111] axis. The angle of this cone decreases with increasing Fe_2O_3 content, and becomes zero at or before pure Fe_2O_3 is reached.

Mössbauer spectroscopy can provide considerable information about the magnetic and crystal field environment of iron-containing systems, and it was in a study of $\alpha\text{-Fe}_2\text{O}_3$ that Kistner and Sunyar (12) first established the existence of the chemical isomer shift and of quadrupole hyperfine interactions. Later, van der Woude (5) carried out a more extensive and extremely careful study of powdered natural $\alpha\text{-Fe}_2\text{O}_3$ and observed a small reduction in the effective magnetic field as the temperature was raised through the Morin temperature (260°K), together with a reversal in the sign of ϵ , the energy shift in the hyperfine levels due to quadrupole interaction. The quadrupole interaction for a number of pure synthetic $\alpha\text{-Fe}_2\text{O}_3$ samples has also been determined in the course of a derivation of the value of the quadrupole moment of ^{57}Fe (13).

Only limited studies of solid solutions of Fe_2O_3 in Cr_2O_3 have been made by means of the Mössbauer effect (14, 15). For 0.035 Fe_2O_3 –0.965 Cr_2O_3 , Srivastava and Sharma (15) have made a number of deductions regarding cone angles and relaxation effects, but in the light of our present results we believe their conclusions to be in error.

We report here Mössbauer data, obtained at a variety of temperatures, for solid solutions of Fe_2O_3 in Cr_2O_3 ranging from 0.2 to 75% Fe_2O_3 . The results are compared with those for $\alpha\text{-Fe}_2\text{O}_3$ – Cr_2O_3 system (11). Effective internal magnetic fields, H_{eff} , at the Fe nucleus have been determined as a function of temperature for each composition, and the nature of magnetic ordering in the system is discussed in terms of H_{eff} values and the observed quadrupole interactions.

Experimental

Preparation of Materials

Solid solutions of 5% or more of Fe_2O_3 in Cr_2O_3 were prepared by mixing and grinding

of the oxides, followed by compaction and heating in air at 1350°C. Each preparation was ground and fired at least twice. Fe_2O_3 was Fisher Scientific Certified Grade, and a pure reactive form of Cr_2O_3 was made by decomposition of analytical grade ammonium dichromate, with final heating of the product at 900°C for 1 hr.

For the samples containing 0.2 and 0.4% of Fe_2O_3 in Cr_2O_3 , iron enriched to 95% in ^{57}Fe was used. For such concentrations standardized solutions of Fe_2O_3 in 5 *N* nitric acid were prepared, and aliquots of these solutions, typically of 1 ml, were added to a weighed quantity of Cr_2O_3 . After careful evaporation to dryness of the resulting slurry, with occasional mixing to prevent segregation, the dried mixtures were heated to 600°C to decompose residual nitrates, and then ground and heated successively at 1000 and 1350°C.

Mössbauer Spectra

The Mössbauer spectra were recorded using Austin Science Associates drive system operating in the constant acceleration mode. Our source was ^{57}Co in a Pd foil which was held at 295°K. The transmitted radiation was detected by a proportional counter, Xe– CO_2 filled at 1 atm, and connected directly to a F.E.T. preamplifier, also supplied by Austin Science Associates. The output from the preamplifier was further amplified, discriminated and stored in a Victoreen PIP 400A multichannel analyser operating in the multiscaler mode. Samples were finely ground powders intimately mixed with apiezon grease and sandwiched in a copper holder between foils of high purity aluminium. These sample holders were rigidly held in a Liquid Transfer Cryotip system manufactured by Air Products and Chemicals Inc., which allowed spectra to be recorded at temperatures from 4 to 300°K. Temperatures were monitored by means of a calibrated iron-doped gold chromel thermocouple and monitored by a Hewlett Packard 419A DC null voltage detector. Spectra above 300°K were obtained by attaching the samples to a copper heat sink partially immersed in a controlled temperature oil bath. In these cases, the temperature of the sample was obtained by means of a copper-constantan thermocouple

TABLE I
 MÖSSBAUER PARAMETERS FOR THE $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ SYSTEM

$\% \text{Fe}_2\text{O}_3$	T (°K)	ΔE^a mm/sec	ε^b mm/sec	H^c_{eff} (kG)	$\% \text{Fe}_2\text{O}_3$	T (°K)	mm/sec ΔE^a	mm/sec ε^b	(kG) H^c_{eff}
100 ^d	0			544		255		—	T_N
	100–220		+0.201			295	0.38		0
	260		0.000	T_M	25	4.2		0.0	532
	295		−0.110 ^e			77		0.0	456
	310–900		−0.103			85		—	417
	956			T_N		111		—	340
	~10000	0.465				122		—	250
	1050	0.49 ^f				149			T_N
				160		0.36			0
75	4.2		−0.12	525	20	4.2		0.0	498
	77		−0.11	528		77		0.0	422
	200		−0.11	515		90		—	392
	295		−0.11	494		117		—	322
	310		−0.11	490		162		—	142
50 ^g	77		−0.10	512	10	175			T_N
	295		−0.11	429		232	0.30		0
	325		−0.10	421		77		+0.08	410
	347		(−0.08)	405		235			T_N
	376		(−0.06)	384		295	0.30		0
40 ^g	4.2		−0.09	510	5	77		— ⁱ	415
	77		−0.10	495		265			T_N
	115		−0.10	485		295	0.27		0
	195		−0.10	455		77		+0.11	438
	222		(−0.08)	439		195		+0.12	283
	273		(−0.05)	393		295		+0.12	89
	295		(−0.08)	371		305		—	T_N
	310		— ^h	355		310	0.27		0
	359		—	266		4.2		+0.10	521
	371		—	222		77		+0.12	440
	390		—	T_N		195		+0.12	284
30	4.2		−0.07	493	0.2	273		+0.13	153
	77		−0.07	466		295		—	93
	181		—	380		305		—	T_N
	200		—	336		330	0.26	—	0
	220		—	296					

^a Quadrupole splitting above T_N .

^b Quadrupole interaction below T_N . Estimated standard deviations ± 0.01 mm/sec except for values in parentheses.

^c Hyperfine field at the Fe nucleus.

^d Data for $\alpha\text{-Fe}_2\text{O}_3$ from van der Woude (5) except where indicated. T_M is the Morin transition temperature, T_N the Néel temperature.

^e Data of Artman et al. (13) for high purity synthetic $\alpha\text{-Fe}_2\text{O}_3$.

^f Data of Ono and Ito (20) for $\alpha\text{-Fe}_2\text{O}_3$ enriched to 60% in ^{57}Fe .

^g For these compositions, values of ε in parentheses indicate uncertain values obtained from broadened spectra.

^h Poor counting statistics from 5% of natural Fe prevented the measurement of ε .

ⁱ Dashed entries indicates spectra too broadened to allow adequate measurements.

attached directly to the sample. Spectra were calibrated by means of a standard iron foil. In nearly all cases, spectra were well defined and were fitted using a computer programme written by Dr. A. J. Stone (16) and modified by Dr. D. H. Grundy of the Department of Geology, McMaster University. However, for the samples in the 5–30% Fe_2O_3 composition range when spectra were obtained near the Néel temperature it was necessary to make visual estimates of the hyperfine field for the broad and ill-defined spectra obtained.

Electron Spin Resonance Measurements

Solid solutions from 0.5 to 5% of Fe_2O_3 in Cr_2O_3 were examined for possible electron spin resonance transitions at temperatures near 300 and at 80°K. Conventional 9 GH spin resonance equipment was used, and sensitivities were sufficient to detect molar concentrations of 0.05% or less of paramagnetic ferric ions in the Cr_2O_3 samples.

Below the Néel temperatures appropriate to each composition no resonances were observed, and we conclude, in accordance with the magnetic behaviour demonstrated by the Mössbauer observations, that the isolated Fe^{3+} ions experience such large ground state splittings that only the lowest ground state level is populated, and spin resonance transitions therefore cannot occur.

Results

Mössbauer spectra were recorded for all composition at temperatures of 77°K and above and also in most instances at 4.2°K. The data obtained are summarized in Table I, where ΔE refers to the quadrupole split above, and ϵ to the quadrupole displacement below, the Néel temperature.

For all concentrations studied, the isomer shift at 77°K was 0.49 ± 0.01 mm/sec, close to the value of 0.47 ± 0.03 for $\alpha\text{-Fe}_2\text{O}_3$ found by Kistner and Sunyar (12). A typical temperature dependence for the isomer shift (5) was observed at all compositions.

Néel Temperatures

Above the transition temperatures for antiferromagnetic ordering, a paramagnetic

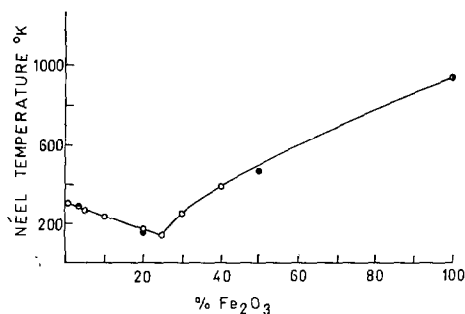


FIG. 1. Variation of Néel temperature with % Fe_2O_3 in Cr_2O_3 ; open circles this work, other points Refs. (5), (14), and (15).

quadrupole-split doublet was observed in all cases. The onset of antiferromagnetism on cooling of the samples was evidenced by a noticeable broadening of the doublet. A plot of these magnetic transition temperatures against composition is shown in Fig. 1 and is very similar to that reported by Cox et al. (11) from neutron diffraction studies. We find the minimum to occur at a composition 0.25 Fe_2O_3 –0.75 Cr_2O_3 in good agreement with their work. The extrapolated value for the Néel temperature of Cr_2O_3 is 305°K, in close agreement with the value obtained by Martin from magnetic data (17), and $306 \pm 2^\circ\text{K}$ found from neutron diffraction measurements (18). Our upper limit of temperature operation was $\sim 400^\circ\text{C}$; however, our data join smoothly to the Néel temperature for $\alpha\text{-Fe}_2\text{O}_3$ of 956°K determined by Mössbauer effect (5).

Hyperfine Spectra

As had been reported for $\alpha\text{-Fe}_2\text{O}_3$ (5) and the Fe_2O_3 – Cr_2O_3 compositions so far examined (14, 15), the hyperfine field increases markedly as the temperature is decreased below the Néel point. For $\alpha\text{-Fe}_2\text{O}_3$ (5, 6), H_{eff} shows a temperature dependence which is the same as for the sublattice magnetization, and extrapolates to a value for H_{eff} at 0°K of 544 kG.

Figure 2 shows the spectra obtained for 0.2% of $^{57}\text{Fe}_2\text{O}_3$ in Cr_2O_3 at a series of temperatures from just above the Néel point down to 4.2°K, and the hyperfine fields obtained at this and each of the other compositions are plotted against temperature in Fig. 3.

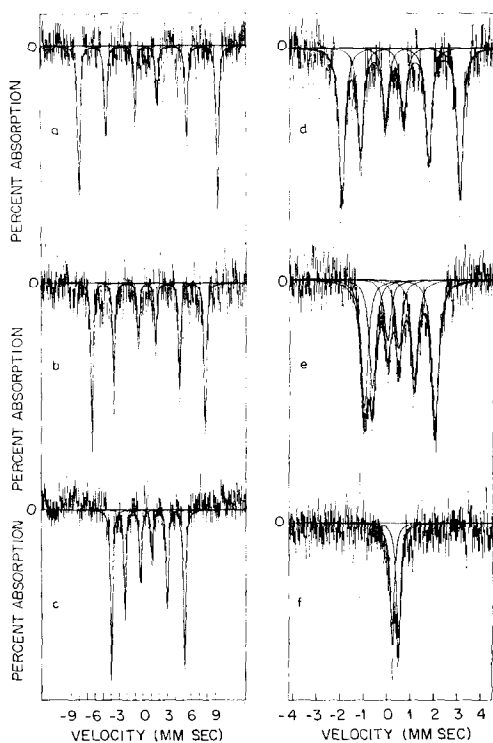


FIG. 2. Mössbauer spectra of 0.2% Fe₂O₃ in Cr₂O₃: (a) 4.2°K, (b) 77°K, (c) 195°K, (d) 273°K, (e) 295°K, (f) 330°K.

Extrapolation of these curves to 0°K show that H_{eff} ($T=0$) varies with composition, decreasing from 544 kG for α -Fe₂O₃ (5) to ~490 kG at the 30% Fe₂O₃ composition. Below 25% Fe₂O₃, H_{eff} ($T=0$) increases to 500 kG at 20% and 525 kG at 0.2% Fe₂O₃, and the curves show a marked change in the temperature dependence of H_{eff} . The 25% sample, which by extrapolation of the values from higher and lower compositions would be expected to show the lowest value, in fact shows an anomalously high value of 530 kG.

Quadrupole Interaction

For the corundum structure type, the electric field gradient (efg) is axially symmetric about [111]. For ⁵⁷Fe in magnetically ordered oxides, quadrupole interactions are small compared with magnetic dipole interaction, and for this situation the theoretical displacements due to the quadrupole interaction with

the excited state levels of the ⁵⁷Fe nucleus are given (19) by

$$\varepsilon = (e^2qQ/4) \left(\frac{3 \cos^2 \theta - 1}{2} \right) \quad (1)$$

where $-e$ is the charge on the electron, eq ($\equiv V_{zz}$) is the negative of the symmetry axis component of the efg tensor, Q is the quadrupole moment and θ is the angle between V_{zz} and the direction of electronic spin quantization. Energy level diagrams showing the quadrupole displacements from the Zeeman level positions of the Mössbauer effect peaks are given for example by van der Woude (5). Displacements are all equal, and the experimental value of ε is found (13) from

$$\varepsilon = 1/8[2(x_1 + x_6) - x_2 + x_3 + x_4 + x_5] \quad (2)$$

where x_i denotes the line position. For $\theta = 90^\circ$, as for α -Fe₂O₃ above the Morin transition, the spin axis is perpendicular to [111], and from Eq. (1),

$$\varepsilon = -(1/8)e^2qQ. \quad (3)$$

For the spin axis parallel to the efg axis, $\theta = 0^\circ$, and

$$\varepsilon = +\frac{1}{4}e^2qQ. \quad (3)$$

In his very careful study on natural α -Fe₂O₃ crystals, van der Woude found for $T > T_M$, $\varepsilon = -0.103$ mm/sec (4.96×10^{-9} eV) and for $T < T_M$, $\varepsilon = 0.210$ mm/sec (9.63×10^{-9} eV), in close agreement with the values expected from Eqs. (3) and (4). Ono and Ito (20) obtained qualitatively similar results.

Although there is a sharp change in H_{eff} of 8 kG on passing through T_M , attributed (5) to small changes in the orbital and dipolar asymmetries of the $3d^5$ spin system with change of spin axis in the presence of an efg directed along [111], the results indicated that within experimental error there is no change in the efg itself.

Our spectrum for 0.75 Fe₂O₃-0.25 Cr₂O₃ taken at 77°K is given in Fig. 4. It shows clearly the presence of a quadrupole interaction, with the separation between lines 1 and 2 being greater than that between lines 5 and 6. Thus, ε is negative, as for α -Fe₂O₃ above T_M (5, 13) and the spins are very close to being perpendicular to [111], since the value for ε , -0.11 ± 0.01 mm/sec, is identical with that found for

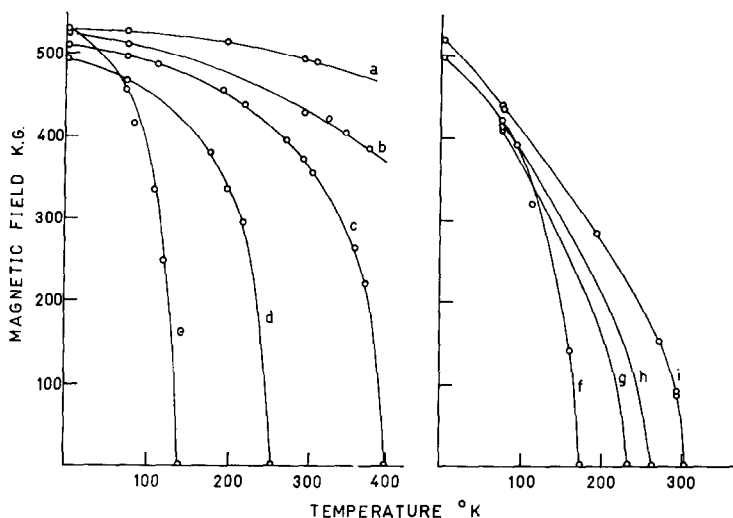


FIG. 3. Temperature variation of hyperfine field for various compositions of Fe_2O_3 in Cr_2O_3 . (a) 75%, (b) 50%, (c) 40%, (d) 30%, (e) 25%, (f) 20%, (g) 10%, (h) 5%, (i) 0.4, and 0.2%.

pure $\alpha\text{-Fe}_2\text{O}_3$ at 295°K (13). Within experimental error ε is constant from 4.2 to 310°K (Table I) and for 75% of Fe_2O_3 the spin axis thus remains perpendicular to $[111]$ over the entire temperature range with no spin-flip transition occurring. In accord with this observation, the internal field H_{eff} increases smoothly with decrease in temperature, Fig. 3, and shows no discontinuity corresponding to such a Morin transition.

For both 50 and 40% Fe_2O_3 , the value of ε

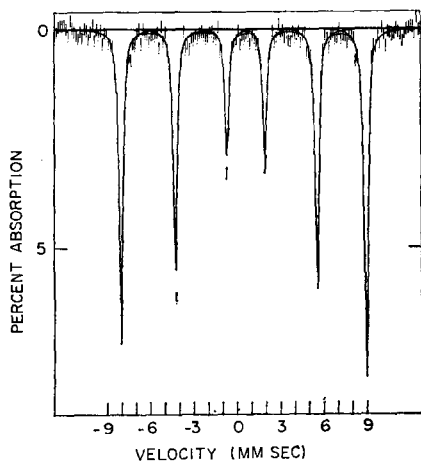


FIG. 4. Mössbauer spectrum of 75% Fe_2O_3 in Cr_2O_3 at 77°K .

is still only slightly lower than for Fe_2O_3 , neglecting the more uncertain values for higher temperature ranges given in parentheses in Table I. For these compositions the cone half-angle β is still close to zero (Table II). Only below 40% Fe_2O_3 does β become significant, and between 30 and 20% where the spiral cone axis becomes parallel with $[111]$, ε falls to zero, Table I. At 10% Fe_2O_3 , $\varepsilon = 0.08$ and at the lowest levels, 0.4 and 0.2% of Fe_2O_3 (enriched to 95% in ^{57}Fe), reaches a final value of 0.113 ± 0.010 mm/sec. The variations in ε observed for the 0.2 and 0.4% samples (Table I) are believed primarily to be due to experimental factors such as variations in the precision of measurement with line separation (Fig. 2). However, a small change in efg as the interatomic spacings change with temperature would not be unexpected (13). There is no evidence for the collapse of the quadrupole interaction with increasing temperature, as Srivastava and Sharma have claimed (15). However, their spectra were considerably less resolved, and their derived values of ε are in considerable doubt.

The final value of ε corresponds, for the efg parallel to $[111]$, to a quadrupole coupling constant of 0.45 ± 0.04 , approximately half that found for $\alpha\text{-Fe}_2\text{O}_3$ 0.880 (13). The efg experienced by isolated Fe^{3+} ions in Cr_2O_3

TABLE II

QUADRUPOLE SHIFTS AND SPIN-CONFIGURATIONS IN $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ SOLID SOLUTIONS

%Fe ₂ O ₃	ϵ^a	β^b	
		Mössbauer	Neutrons
0.2	0.113 ± 0.010	0,	0,
10	0.08 ± 0.01	26 ± 4 ,	40,
15	—	—	66,
20	0.00 ± 0.01	55 ± 4 ,	71, \perp
25	0.00 ± 0.01	55 ± 4 , \perp	51, \perp
30	-0.07 ± 0.01	40 ± 6 , \perp	35, \perp
35	—	—	19, \perp
45 ^d	-0.100 ± 0.005	14 ± 4 , \perp	—
75	-0.110 ± 0.005	0 ± 10 , \perp	—
100 ^e	-0.110 ± 0.003	0, \perp	0, \perp

^a From Table I.^b β is the cone half-angle. For cone-axis parallel to [111], e^2qQ is assumed to be that for the 0.2% Fe₂O₃ composition, +0.448. For cone axis perpendicular to [111], e^2qQ is assumed to be that for $\alpha\text{-Fe}_2\text{O}_3$, +0.880.^c Cox, Takei, and Shirane (11).^d Average of 40 and 50% values.^e Artman (13).

is thus half that in $\alpha\text{-Fe}_2\text{O}_3$. The paramagnetic quadrupole splittings ΔE (Table I), which are also presumed to be relatively insensitive to sample temperature, show a similar ratio, 0.26 mm/sec for 0.2% Fe₂O₃ in Cr₂O₃ at 330°K and 0.465 mm/sec at 1000°K for $\alpha\text{-Fe}_2\text{O}_3$ (5).

The calculations of Artman *et al.* (13) on the effect of the z parameter on the product e^2qQ show that a change of z parameter for Fe³⁺ in Fe₂O₃ from 0.3553 to an assumed value of 0.359 would be sufficient to reduce the value of e^2qQ by half, as we observe. This corresponds to a movement of 0.051 Å by the Fe³⁺ ion away from the Cr³⁺ position and towards the unoccupied octahedral site, and is consistent with the requirement of fitting the Fe³⁺ ion, $r_{\text{Fe}^{3+}} = 0.645$ Å, into the Cr₂O₃ lattice, $r_{\text{Cr}^{3+}} = 0.615$ Å (22). A comparable movement of Cr³⁺ ions by 0.06 Å in chromia-containing Al₂O₃ has been demonstrated by Moss and Newnham (21).

Discussion

The Mössbauer spectra for the Fe₂O₃-Cr₂O₃ system are consistent with the spiral

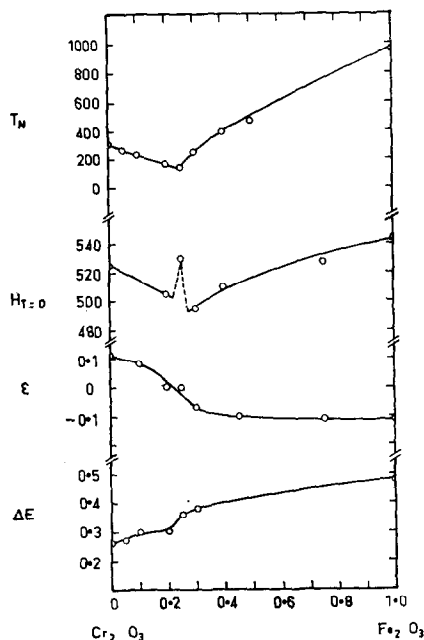


FIG. 5. Concentration dependence of T_N , $H_{\text{eff}}(T=0)$, ϵ and ΔE for the $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ system.

spin-ordering models based on neutron diffraction results (1) and provide direct evidence for the progressive change of spin direction from parallel to [111] to perpendicular to [111] as the composition is changed between the end members Cr₂O₃ and Fe₂O₃. From the data in Table I and the curves in Fig. 5 it is seen that the minimum in T_N at 25% Fe₂O₃ corresponds to discrete changes in the other Mössbauer parameters. These results indicate that the transition from a predominantly Cr₂O₃ type spin-ordering to one based on Fe₂O₃ occurs in the region of 25% Fe₂O₃ rather than 15–20% as suggested by Cox *et al.* (11). In addition, a detailed calculation of cone half-angles over the composition range, Table II, shows that the cone half-angle, at least for the Fe³⁺ ions, increases more slowly and to less extreme values than indicated by the neutron diffraction models. These latter are based primarily on the intensities of peaks satellite to the main magnetic peaks of Cr₂O₃ and Fe₂O₃ and incorporate a definite statistical uncertainty. Furthermore, the spiral models were chosen on the basis of one predominant interaction

between neighbouring metal atoms, and subsequent inelastic neutron scattering investigations (6, 10) show that there are two comparable interactions in each of Cr_2O_3 and Fe_2O_3 . Inclusion of the additional interactions could well alter the details of the spin-spiral models, including the composition point at which spin-ordering changes.

It should be noted that for cone axes perpendicular to [111], a value of ϵ will be obtained which is the result of averaging all of the possible values of $(\cos^2\theta - 1)$ which correspond to rotation of the spin about the cone axis. Individual values of θ are given by

$$\sin(90 - \theta) = \sin\beta \sin\phi,$$

where θ is the angle between the [111] axis and the spin direction, β is the cone half-angle and ϕ is the angle by which the spin is turned out of the [111] plane. Trial calculations show that the averaged value of $(3 \cos^2\theta - 1)$ for any such distribution is within a few percent of the simple average between the extreme values for $\theta = (90 - \beta)^\circ$ and for $\theta = 90^\circ$. The broadening of the spectra for the 20–40% compositions at temperatures above $\sim 0.5 T_N$ is consistent with rapid relaxation of spin directions about particular cone axes.

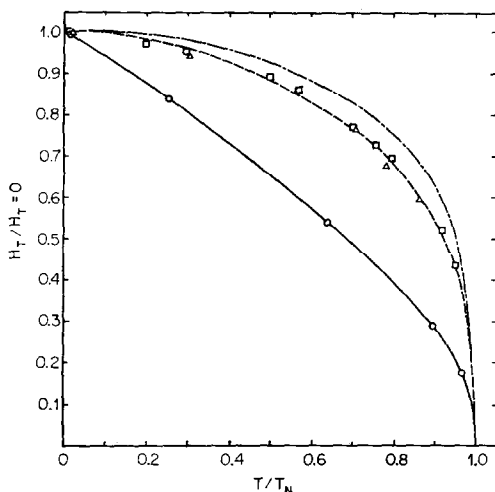


FIG. 6. Experimental values of $H_{\text{eff}}(T)/H_{\text{eff}}(T=0)$ vs T/T_N for the Fe_2O_3 - Cr_2O_3 system: (---) Cr_2O_3 , neutron diffraction (10, 18); (-·-) α - Fe_2O_3 , neutron diffraction (6) and Mössbauer effect (5); (—) 0.2% of $^{57}\text{Fe}_2\text{O}_3$ in Cr_2O_3 ; triangles: Fe_2O_3 content of 30%; squares: Fe_2O_3 content of 40%.

The Fe_2O_3 - Cr_2O_3 system shows a typical decrease in Néel temperature with dilution of Fe_2O_3 content (22) (Fig. 1) and the internal field at the nucleus also fall as the composition changes from 100% Fe_2O_3 down to 30% Fe_2O_3 . If Cr_2O_3 itself was not antiferromagnetic, T_N would fall to zero near this composition (21). Despite the decrease in T_N , however, a plot of reduced internal magnetic field $H_{\text{eff}}(T)/H_{\text{eff}}(R=0)$ vs T/T_N , Fig. 6, shows that the same temperature dependence is obtained from 100% of a α - Fe_2O_3 down to 30% Fe_2O_3 , and in fact these curves lie essentially on that found for α - Fe_2O_3 (5, 6, 20). The reduced internal magnetic field for α - Fe_2O_3 has been shown (6) to agree closely with the sublattice magnetization $\langle S^z \rangle$ determined by neutron diffraction, and our results are thus closely in accord with the persistence of a dominant Fe_2O_3 -type spin ordering down to 30% of Fe_2O_3 .

It is reasonable to suppose that over the composition range of Fe_2O_3 -type ordering, Fe^{3+} atoms are located at crystallographic positions similar to those in Fe_2O_3 , namely somewhat further displaced from the triad of octahedrally face-shared oxygen atoms than are corresponding metal atoms in a "normal" corundum structure (23). A relatively constant value of the electric field gradient (efg) at Fe^{3+} sites could therefore be expected over this composition range.

At 25% Fe_2O_3 , the $H_{\text{eff}}/H_{\text{eff}}, T=0$ values are somewhat scattered, consistent with this being the transition composition, and at temperatures away from absolute zero are significantly lower than those for the higher Fe^{3+} concentration. At an Fe^{3+} concentration of 0.2%, at which all but a minute fraction of Fe^{3+} ions are isolated from one another (24), even though the zero temperature value of H_{eff} , 525 kG is normal for spin-ordered Fe^{3+} , and the Néel temperature, 305°K, is that of the Cr_2O_3 host lattice, the reduced magnetization curve does not move towards that of Cr_2O_3 (10–18) (Fig. 6) as might have been expected, but falls even further below that for α - Fe_2O_3 . In addition, the curve does not approach zero slope towards zero temperature, but has a negative slope of $\sim 30^\circ$ from 4 to 200°K. This behaviour indicates that the Fe^{3+} ions are

coupled only weakly to the Cr_2O_3 spin lattice, and that their spin alignment shows a much more direct temperature dependence than that of the strongly coupled Cr^{3+} ions.

The differences in d orbital occupation between Cr^{3+} and Fe^{3+} are sufficient to explain a poor superexchange overlap between Fe-O-Cr orbitals (25), and as the main contribution to the internal field at the Fe nucleus arises from polarization of the inner s -electrons by the average z component of the $3d^5$ electronic spin system, full alignment at zero alignment by removal of the Cr_2O_3 internal field at 305°K seems consistent with a weak coupling scheme.

Acknowledgments

The authors are indebted to Mrs. C. Li for assistance in the preparation of samples, and to Professor D. A. Shirley for helpful discussions.

References

1. L. PAULING AND S. B. HENDRICKS, *J. Amer. Chem. Soc.* **47**, 781 (1925).
2. H. E. VON STEINWEHR, *Z. Krist.* **125**, 377 (1967).
3. C. G. SHULL, W. A. STRAUER, AND E. O. WOLLAN, *Phys. Rev.* **83**, 333 (1951).
4. B. N. BROCKHOUSE, *J. Chem. Phys.* **21**, 961 (1953).
5. F. VAN DER WOUDE, *Phys. Status Solidi* **17**, 417 (1966).
6. E. J. SAMUELSON AND G. SHIRANE, *Phys. Status Solidi* **12**, 241 (1970).
7. P. IMBERT AND A. GERARD, *C. R. Acad. Sci. Ser. C* **257**, 1054 (1963).
8. J. A. EATON AND A. H. MORRISH, *J. Appl. Phys.* **40**, 3180 (1969).
9. T. R. MCGUIRE, E. J. SCOTT, AND F. H. GRANNIS, *Phys. Rev.* **102**, 1000 (1956).
10. E. J. SAMUELSON, M. T. HUTCHINGS, AND G. SHIRANE, *Physica* **48**, 13 (1970).
11. D. E. COX, W. J. TAKEI, AND G. SHIRANE, *J. Phys. Chem. Solids* **24**, 405 (1963).
12. O. C. KISTNER AND A. W. SUNYAR, *Phys. Rev. Letters* **4**, 412 (1960).
13. J. O. ARTMAN, A. H. MUIR, JR., AND H. WIEDERSICH, *Phys. Rev.* **173**, 337 (1968).
14. G. SHIRANE, D. E. COX, AND S. L. RUBY, *Phys. Rev.* **125**, 1158 (1962).
15. J. K. SRIVASTAVA AND R. P. SHARMA, *Phys. Status Solidi* **35**, 491 (1969).
16. A. J. STONE, Appendix to G. M. Bancroft, A. G. Maddock, W. K. Ong, and R. M. Prince, and A. J. Stone, *J. Chem. Soc (A)*, 1966 (1967).
17. T. J. MARTIN, *Phys. Letters* **17**, 83 (1965).
18. H. SHAKED AND S. SHTRIKMAN, *Solid State Comm.* **6**, 425 (1968).
19. G. K. WERTHEIM, "Mössbauer Effect: Principles and Applications," chap. vii, Academic Press Inc., New York, 1964.
20. K. ONO AND A. ITO, *J. Phys. Soc. Japan* **17**, 1012 (1962).
21. S. C. MOSS AND R. E. NEWNHAM, *Z. Krist.* **120**, 359 (1964).
22. A. F. REID, T. M. SABINE, AND D. A. WHEELER, *J. Solid State Chem.* **4**, 400 (1972).
23. C. T. PREWITT, R. D. SHANNON, D. B. ROGERS, AND A. W. SLEIGHT, *Inorg. Chem.* **8**, 1985 (1969.)
24. J. FERGUSON AND P. E. FIELDING, *Aust. J. Chem.* **25**, 1371 (1972).
25. W. P. OSMOND, *Proc. Phys. Soc.* **79**, 394 (1962).