Mössbauer-effect investigation of iron–chromium oxide systems

Mössbauer effect investigations on α-$Fe_2O_3 \cdot Cr_2O_3$ solid solutions have been reported by several workers [1–8]. The samples had been usually prepared by heating mixtures of individual metal oxides at high temperatures [1–7]. Since the influence of varying the relative concentration of component oxides on the nature and properties of solid solutions formed has not been well studied so far, further Mössbauer studies are made on the system covering a wider concentration range.

Iron–chromium oxide samples were prepared by annealing the Fe–Cr co-precipitated hydroxides. Sodium hydroxide (A.R.) solution was slowly added in slight excess to a rapidly stirred and freshly prepared mixture of Fe(III) and Cr(III) salt solutions at room temperature. The concentrations of the chloride solutions were adjusted so that the weight percent ratio of Fe to Cr varied as 1:9, 3:7, 1:1, 7:3 and 9:1. The precipitated gels were washed with distilled water until free from electrolyte and were air-dried at room temperature. The air-dried samples were heated at 800° C for 4h in a muffle furnace and cooled slowly to room temperature. For comparison samples of α-Fe_2O_3 and Cr_2O_3 were obtained by heating their hydroxide gels precipitated at room temperature from their chloride solutions at 800° C for 4h. Mössbauer spectra of α-Fe_2O_3 and mixed-oxide systems were recorded with a ^{57}Co source in a Pd-matrix in standard transmission geometry. Iron metal was used for velocity calibration and as the standard for the centre-shift data. The centres of all the spectra depicted in Fig. 1 are with respect to iron.

Mössbauer spectra at 300K and parameters obtained therefrom for the mixed-oxide systems, together with that of α-Fe_2O_3, are given in Fig. 1 and Table I, respectively. Samples 1 and 2 each gave a well-resolved paramagnetic doublet spectrum while samples 3, 4 and 5 resembled spin-ordered hyperfine magnetically split spectra of α-Fe_2O_3. Mössbauer parameters of all these samples irrespective of their composition, characterize iron atoms in the high-spin ferric state in distorted octahedral sites. Vacancies, lattice strains and structural inhomogeneities that may be present in the system are accounted for by the broadening of resonance lines while the observed symmetry arises from the possible relaxation effects.

Subtle variations in Mössbauer parameters of the samples reflect changes in electronic environment of iron ions. Compared to the value of isomer shift (I.S.) for α-Fe_2O_3, I.S. data for samples 2, 3, 4 and 5 show small but distinct increments indicating a trend towards an increase in ionicity of iron (III)–oxygen bonds due to the varying extents of Cr^{3+} substitution. An explanation of this might be that the smaller Cr cation attracts oxygens from the neighbouring Fe–O_6 octahedra thereby lengthening the Fe–O_6 bonds. The I.S. of sample 1 is smaller than that observed for α-Fe_2O_3 and clearly indicates a distinct degree of co-valency in iron–oxygen bonds for iron ions incorporated in α-Cr_2O_3 lattice. For quadrupole splitting the contribution to electric field gradient is from the lattice ions surrounding the Fe^{3+} ions, and the magnitude of this contribution in the rhombohedral Cr_2O_3–Fe_2O_3 lattice will depend on its trigonality, i.e. on the ratio c/a where c and a are the lattice parameters [6]. Furthermore, a preliminary X-ray diffraction

TABLE I ^{57}Fe-Mössbauer parameters at 300 K of the iron–chromium oxide system

Sample number	Composition (wt %) Fe:Cr	Colour	I.S. λ/Fe (mm sec^{-1})	Q.S. ΔE_Q (mm sec^{-1})	H.F.S. H_n (kOe)
1	1:9	Greyish brown	0.33	0.32	–
2	3:7	Blackish brown	0.39	0.40	–
3	1:1	Greyish black	0.36	0.13	472
4	7:3	Brown	0.43	0.04	506
5	9:1	Dark brown	0.39	0.16	506
6	10:0 (α-Fe_2O_3)	Reddish brown	0.35	0.12	516

Isomer shifts are with respect to Fe metal foil. Error in I.S. and Q.S. is ± 0.04 mm sec^{-1} and over H_n it is ± 2.5 kOe.

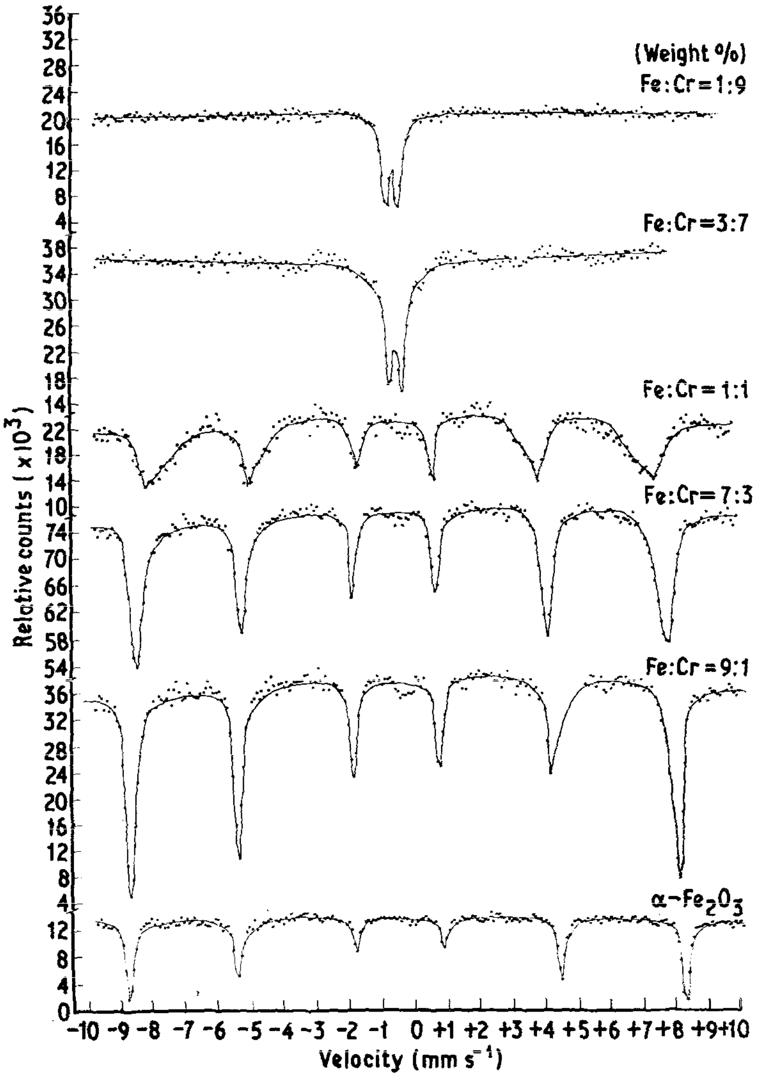

Figure 1 Mössbauer spectra of iron–chromium oxide systems at 300 K containing iron and chromium in the ratio (wt %) 1:9, 3:7, 1:1, 7:3 and 9:1, and α-Fe_2O_3.

examination of samples indicated that substitution of chromium in haematite structure results in a differential disorder in the crystal lattice and that all lines show a significant shift towards lower spacings. The observed increase in quadruple splitting may be related to a corresponding increase in the lattice parameters of microcrystalline α-Fe_2O_3 due to a decrease in the particle size of the iron oxide component. Thus, depending on the different extents of incorporation of Cr(III) ions for Fe(III) ions and trigonality of the system, quadrupole splitting ranges from 0.04 to 0.40 mm sec^{-1}. The values of Q.S. for samples 3, 4 and 6 are close to that of α-Fe_2O_3 while those of samples 1 and 2 are in conformity with the data reported earlier [1, 8]. The latter is attributed to large lattice contributions to the electric field gradient of iron ions arising from distant charges and asymmetric surfaces of the host α-Cr_2O_3 lattice for which cation displacement from octahedron centres and bond angles smaller than α-Fe_2O_3 metal–metal distance are reported [9].

The antiferromagnetic character of α-Fe_2O_3 ($T_N = 955$ K) is brought about by spin–spin interaction along Fe–O–Fe bridges by a super-exchange mechanism while the antiferromagnetism of α-Cr_2O_3 ($T_N = 308$ K) is brought about by a weak direct spin–spin interaction between Cr^{3+} ions over common faces and edges leading to relatively short Cr^{3+}–Cr^{3+} distances (2.65 Å) along the hexagonal axis [6].

In the samples studied here, small particle size and increased incorporation of Cr ions both contribute to subnormal effective internal magnetic fields. In summary, starting with a solid solution of iron ions incorporated in a Cr_2O_3 lattice (sample 1), increasing Fe content results in the formation of super paramagnetic clusters of iron ions which are initially held on the surfaces of chromia hosts with a low symmetry of crystal field around them still resulting in the doublet character of Mössbauer spectra (sample 2). With further increase in the iron oxide component, the iron ion clusters grow in size and develop crystallinity although retaining, to some extent, the inhibiting effects due to chromium ions in the α-Fe_2O_3 lattice, as has been shown by magnetically ordered spectra with subtle diminutions in H_n values.

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X-ray topographic assessment of flux-grown crystals of rare earth germanates ($R_2Ge_2O_7$)

The growth of single crystals of the tetragonal rare earth germanates from a flux of R_2O_3, PbO, PbO_2, GeO_2 and PbF_2 was first reported by one of us in 1973 [1]. In subsequent experiments, the flux was modified to contain a large excess of GeO_2, and MoO_3 was added as a major component. With this composition, it was possible to reduce flux evaporation and to allow crystals to grow by slowly cooling the melt. Large, optically clear, equidimensional crystals of $R_2Ge_2O_7$ were obtained, up to 3 mm x 3 mm x 3 mm, and basal plates up to 5 mm x 5 mm x 1 mm thick, some of which were free from visible inclusions [2]. In this communication, the study of a substantial number of such platelets by X-ray topography is briefly reported.

As-grown crystals of plate-like habit, leached from the flux, were selected on the basis of optical perfection and were examined without cutting or polishing. For $AgK\alpha_1$ radiation, the product of absorption coefficient and thickness, μt, was typically 2 to 10.

All the crystals examined were bent. Only the crystal shown in Fig. 1 was sufficiently uniform for Lang topographs to be taken, and here only one reflection could be obtained. Lang topographs, which rely on collimated characteristic radiation, could not be taken of the others and, because the bending was about two orthogonal axes, a Bragg angle controller proved little use. Very rapid

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