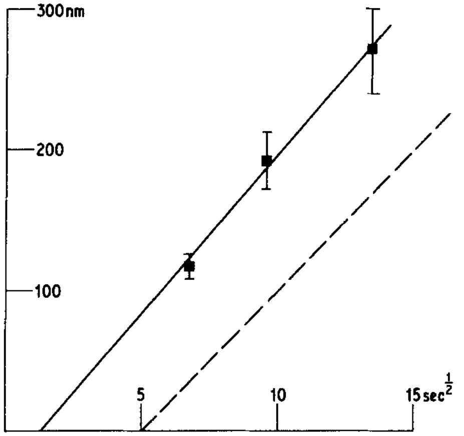

Figure 2 Oxide thickness plotted against the square root of time. The full line is constructed using oxide thicknesses derived from Fig. 1 and the dashed line is taken from [1]. Note that the re-estimated oxide thicknesses obtained from Fig. 1 are considerably larger.

oxidation at 500° C. These thicknesses may be compared because the oxidation rate is fairly independent of O_2 pressure at these initial stages.

These underestimation of oxide thicknesses [1] occurred because the calibration points used relate to the attenuation of electrons, emanating from stainless steel substrates, in iron overlayers rather than iron oxide overlayers on iron. For electrons with energy of ~ 5 keV the linear attenuation coefficients can be taken to be inversely proportional to the density of the matrix and it is, therefore, to be expected that a thicker oxides thicknesses of 280 nm and 250 nm at 10^{-3} and 10 Torr O_2 pressure, respectively, for 180 sec iron overlayer [6]. This is clearly seen by reference to the figures.

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M. J. TRICKER
Department of Chemistry,
Heriot-Watt University,
Riccarton, Currie,
Edinburgh, UK

Application of the Mössbauer effect to the characterization of the mixed valence compound α-Rb_xFeF_3

The magnetic properties of a number of complex fluorides of transition metals have been studied previously by means of the Mössbauer effect. Here, the application of the Mössbauer effect to the characterization of a mixed valence compound, α-Rb_xFeF_3 ($0.18 < x < 0.29$) [1, 2] is reported. The structure [1] of this insulating material is very similar to that of $Rb_2Fe_5F_{17}$, both closely resembling that of the tungsten bronze, α-M_xWO_3 [3] (M = K, Rb, Cs). The X-ray powder patterns have identical *d*-values and similar intensities except for a few of the weaker lines [4]. Thus it is very difficult to distinguish between α-Rb_xFeF_3 and $Rb_2Fe_5F_{17}$ by the X-ray powder method. According to the formula α-Rb_xFeF_3 ($0.18 < x < 0.29$), iron is present as both Fe^{2+} and Fe^{3+}. Mössbauer measurements were made on a single crystal grown by the flux method [5]. ^{57}Fe Mössbauer spectra were recorded with a conventional constant acceleration spectrometer, using ^{57}Co (Rh) source. The spectra were computer fitted by means of a modified program [6].

A room temperature Mössbauer spectrum of Rb_xFeF_3 is shown in Fig. 1. It consists of two quarupole doublets as indicated in the figure. The longer doublet is due to high spin Fe^{3+} on the basis of its isomer shift, 0.56 mm sec^{-1}; and the quadrupole splitting, 0.58 mm sec^{-1} [7] (relative to metallic iron). The isomer shift and the quadrupole splitting of the second doublet is less well determined because one of its absorption peaks is hidden, but possible values of the isomer shift and the quadrupole splitting are 1.43 and 2.77 mm sec^{-1}, respectively, which are typical values for high spin Fe^{2+} [7]. The broadness of the Fe^{2+} lines presumably arises from inhomogeneous quad-

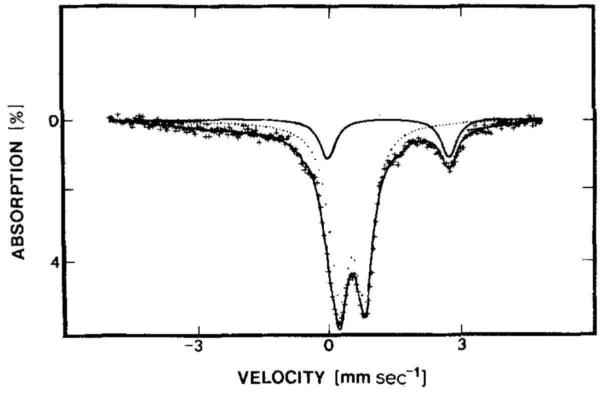

Figure 1 ^{57}Fe Mössbauer effect absorption spectrum of Rb$_x$FeF$_3$ at 293 K. The absorption due to Fe^{2+} is shown by a continuous line.

rupole effects. The electric field gradient at the nucleus in Fe^{2+} depends on the crystal field splitting of the 3*d*-electrons, which is affected by the random position of the rubidium neighbours and by the distribution of the valence of the iron neighbours.

The Mössbauer spectrum at 4.2 K is shown in Fig 2, and suggests that below the Néel temperature the spectrum of Fe^{3+} exhibits narrow lines while the spectrum of Fe^{2+} merges into the background, with only a few discernible features. The hyperfine field of Fe^{3+} is 578 kOe, a value less than the field of FeF$_3$ in which the iron has an undistorted octahedral environment. The area under the two absorption peaks was used to determine the valence ratio Fe^{2+} :Fe^{3+} [8], which was found to agree with the formula Rb$_{0.18}$FeF$_3$ (within 0.5% accuracy). The relatively narrow Fe^{3+} absorption peaks suggest that the trivalent atoms all occupy equivalent sites, in accordance with the proposed [4] tunsten bronze type structure. This study thus shows that the Mössbauer method provides a rapid, accurate and non-destructive method of determination of the valence ratio in iron compounds.

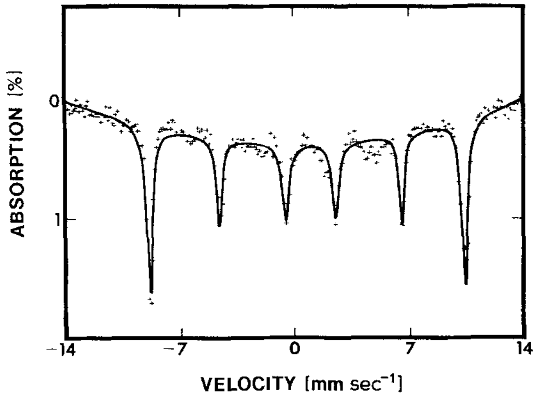

Figure 2 Mössbauer absorption spectrum of Rb$_x$FeF$_3$ at 4.2 K. The absorption due to Fe^{2+} merges into the background.

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ASGHARI MAQSOOD*
Clarendon Laboratory,
Oxford,
UK

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*Permanent address: Physics Department, Quaid-i-Azam University, Islamabad, Pakistan.