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Iron-57 Mössbauer Effect Study of the Distribution of Divalent and Trivalent Ions in Potassium Transition Metal Fluorides Having the Tetragonal Bronze Structure

E. BANKS* AND G. TORRE†

Department of Chemistry, Polytechnic Institute of New York, Brooklyn, New York 11201

AND J. A. DELUCA

General Electric Corporate Research and Development, Schenectady, New York 12301

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Mössbauer studies are reported for compounds of the type $KM^{II}M^{III}F_6$ (M = first-row transition metal ion, Zn, or Mg) which have the tetragonal bronze structure. The results of this investigation provide evidence that the trivalent ions are located on the 8(*j*) sites of the bronze structure and that the divalent ions are distributed over both the 8(*j*) and 2(*c*) sites.

Introduction

Since dePape's (*1*) report that $KFe^{II}Fe^{III}F_6$ ($K_{0.5}FeF_3$) has the tetragonal bronze structure (*2*), there have been prepared a number of similar tetragonal fluorides, such as the materials $KM^{II}Fe^{III}F_6$ (M = Mn, Co, Ni, Zn, Mg) and $KM^{II}Cr^{III}F_6$ (M = Mn, Fe, Co) reported by Hardy *et al.* (*3*).

In their Mössbauer effect study of $K_{0.5}FeF_3$ Buchanan *et al.* (*4*) infer from the linewidth data that the Fe^{3+} ions are on equivalent sites and that the Fe^{2+} ions are distributed over nonequivalent sites. Greenwood *et al.* (*5*) feel that the arguments based on linewidth data are not convincing because their 4.2°K Mössbauer spectra of $K_{0.4}FeF_3$ (also tetragonal) show an asymmetry in the outer lines of the Fe^{3+} magnetic hyperfine pattern which they interpret as evidence that the Fe^{3+} ions are not on equivalent sites, or at the very least, not equivalent over short distances. Both groups are restricted to interpretations based on linewidths and small asymmetries in an otherwise distinct magnetic hyperfine pattern because in neither their room- nor their low-temperature spectra is there direct evidence of absorption profiles arising from iron-ions of like charge occupying crystallographically nonequivalent sites. The room-temperature spectra of $K_{0.5}FeF_3$ and $K_{0.4}FeF_3$ can be described as an Fe^{3+} doublet with somewhat broadened linewidths and an Fe^{2+} doublet with very broad symmetrical absorption profiles one of which is totally unresolved as it is directly superimposed on the Fe^{3+} doublet. At

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* Author to whom correspondence should be addressed.

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low temperatures one finds a single distinct Fe^{3+} magnetic hyperfine spectrum and a broad unresolved Fe^{2+} spectrum.

We began a Mössbauer effect study of selected compositions of "tetragonal bronze" fluorides in an effort to obtain direct evidence for the distribution of ions originally proposed by Buchanan *et al.* which we believed (*6*) was consistent with the limited data available. We reasoned that if the Fe^{2+} ions were on non-equivalent sites as proposed, then because of the sensitivity of the Mössbauer parameters of Fe^{2+} to changes in the local environment we might be able to prepare "tetragonal bronze" fluoride compositions in which the differences in the local environments of the 8(*j*) and 2(*c*) sites would be sufficient to result in a Mössbauer spectrum in which the contributions from the two kinds of Fe^{2+} ions are clearly resolved. By comparing the areas under the resolved spectra we could obtain a direct measure of the relative site occupancy.

Experimental

The tetragonal materials $KM^{II}M^{III}F_6$ were prepared by the method previously reported (*6, 7*).

Mössbauer effect measurements were made on samples containing 10 mg Fe/cm^2, using a 10-mc Co^{57} in Pd source. An Elscint spectrometer (Model MD-3 transducer driven by a Model MFG-3A function generator) was used in the constant acceleration mode in conjunction with a Northern Scientific Model NS-900 multichannel analyzer. The spectrometer was calibrated with an α-iron foil, and a sodium nitroprusside standard was used as an isomer shift reference. A Ricor cryogenics attachment was used for measurements at 77°K. The spectra were computer fitted with the NBS program (*8*).

Results

A room-temperature Mössbauer spectrum typical of the samples containing Fe^{3+} and no Fe^{2+} is shown in Fig. 1a. All the Fe^{3+} spectra show a doublet with linewidths broader than the natural linewidth. The room-temperature spectrum of $K[Fe_{0.4}Mg_{0.6}]VF_6$ shown in Fig. 1b clearly shows spectra arising from two kinds of Fe^{2+} ions. The spectra for the other samples prepared to contain Fe^{2+} only are similar but differ in details such as the degree of overlap of the two Fe^{2+} spectra and the relative intensities of the peaks. The spectrum of $K[Fe_{0.4}Mn_{0.6}]FeF_6$ which contains both Fe^{2+} and Fe^{3+} is similar to the spectra reported for $K_{0.5}FeF_3$ and $K_{0.4}FeF_3$ with the exception that the higher velocity members of the Fe^{2+} profiles are resolved and do not combine to form a single very broad symmetrical absorption.

In analyzing the data we used the curve-fitting routine to fit only the absorption profiles that were clearly present to visual inspection. The probable errors listed along with the data in Table I are determined from those calculated for the various parameters of these curves as fit by the program. Inspection of the area fraction data for the Fe^{2+} spectra reveals an asymmetry between the lower velocity components and the higher velocity components. This asymmetry is due to the presence of an unresolved Fe^{3+} impurity spectrum which coincides with the lower velocity components of the Fe^{2+} spectra. At 77°K this impurity spectrum can be partly resolved, the effect being most pronounced in the sample $KFe^{II}_{1.4}Mn^{II}_{0.6}Cr^{III}F_6$ as shown in Fig. 2. In those instances where the overlap of Fe^{2+} and Fe^{3+} does not permit resolution of the component peaks, only approximate values of peak position-dependent parameters (isomer shift and quadrupole splitting) are listed in Table I. These are identifiable as the entries made without a corresponding error estimate. However, it can be seen that the isomer shift and quadrupole splitting values are typical of Fe^{3+}- and Fe^{2+}-containing fluorides. The higher velocity components of the Fe^{2+} spectra are not distorted by impurity contributions and the ratios listed in Table II can be used as a measure of the relative occupancy of the Fe^{2+}

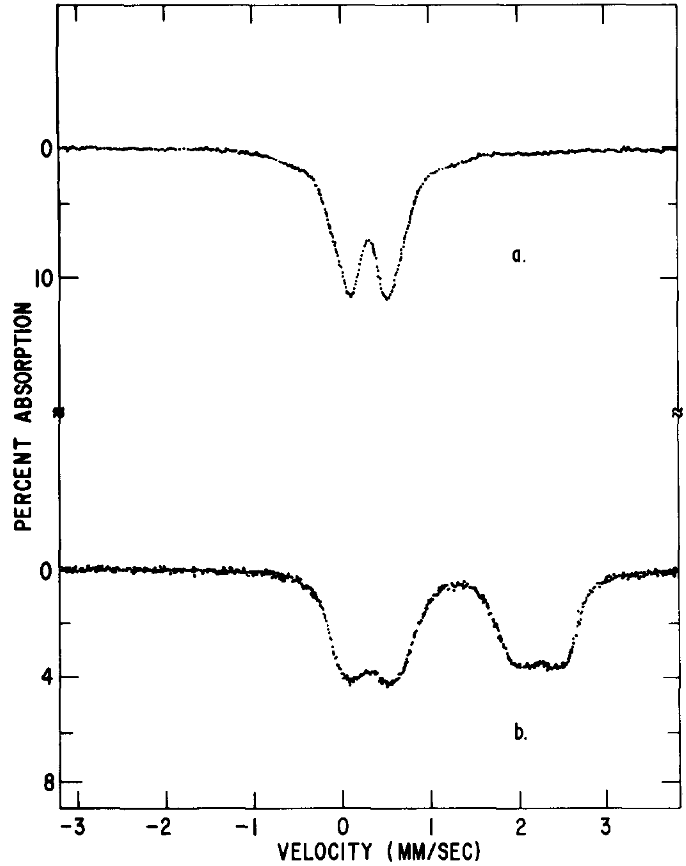

FIG. 1. Room-temperature Fe^{57} Mössbauer spectra of (a) $KCoFeF_6$ and (b) $K[Fe_{0.4}Mg_{0.6}]VF_6$.

ions on the nonequivalent sites of the tetragonal structures. The values given in Table II are computed by taking the ratio of the larger to the smaller of the undistorted higher velocity Fe^{2+} absorptions.

Discussion

There are five formula units, $KM^{II}M^{III}F_6$, per unit cell in the tetragonal bronze structure, and the ten multivalent ions (i.e., $5M^{II}$, $5M^{III}$) per unit cell fill the eight $8(j)$ and two $2(c)$ sites. If there is no site preference and both the divalent and trivalent ions distribute themselves randomly over the available sites, then the areas under the two Fe^{2+} spectra, resulting from Fe^{2+} on two different sites, should be in the ratio of 8:2. If the multivalent ions are distributed in the manner proposed by Buchanan *et al.*, then the M^{3+} ions must occupy five of the eight $8(j)$ sites (per unit cell) and the M^{2+} ions must then fill the remaining three $8(j)$ sites and two $2(c)$ sites. That is, if there exists the site preference proposed for the trivalent and divalent ions, then the areas under the Fe^{2+} absorptions for the two sites should be in the ratio of 3:2, such a ratio being obtainable only for the arrangement of ions proposed by Buchanan *et al.* (provided the Mössbauer fractions are equivalent).

We see in Table II that the area ratios measured for samples in which two Fe^{2+} spectra are resolved are ~3:2 for three of the samples and 5:4 for the remaining two samples. Thus, the data clearly indicate that there is a site preference for the divalent and trivalent ions and the area ratios measured

TABLE I

ROOM TEMPERATURE MÖSSBAUER PARAMETERS[a]

$KM^{II}M^{III}F_6$	Isomer shift[b]	Quadrupole splitting	Line half-widths[c]	Area fraction of total
$KZnFeF_6$	0.764 (±0.013)	0.504 (±0.022)	0.426 (±0.029)	0.50
			0.440 (±0.029)	0.50
$K_{0.9}[Mn_{0.4}Mg_{0.5}]Fe_{1.1}F_6$	0.719 (±0.005)	0.489 (±0.006)	0.376 (±0.008)	0.50
			0.368 (±0.008)	0.50
$KMnFeF_6$	0.721 (±0.005)	0.423 (±0.006)	0.341 (±0.007)	0.50
			0.333 (±0.007)	0.50
$KMgFeF_6$	0.716 (±0.005)	0.527 (±0.006)	0.447 (±0.007)	0.50
			0.452 (±0.007)	0.50
$KCoFeF_6$	0.723 (±0.005)	0.466 (±0.006)	0.386 (±0.008)	0.50
			0.379 (±0.008)	0.50
$KFeVF_6$	1.60	2.21	0.401 (±0.015)	0.18
			0.426 (±0.016)	0.19
	1.63	1.38	0.542 (±0.014)	0.36
			0.489 (±0.015)	0.28
$KFeCrF_6$	1.61	2.10	0.408 (±0.012)	0.27
			0.421 (±0.013)	0.25
	1.65	1.47	0.438 (±0.012)	0.30
			0.388 (±0.015)	0.18
$K[Fe_{0.4}Mg_{0.6}]VF_6$	1.73	2.48	0.451 (±0.013)	0.26
			0.413 (±0.014)	0.20
	1.63	1.35	0.488 (±0.013)	0.29
			0.482 (±0.015)	0.25
$K[Fe_{0.4}Mn_{0.6}]CrF_6$	1.61	2.19	0.359 (±0.012)	0.33
			0.337 (±0.017)	0.20
	1.67	1.49	0.406 (±0.013)	0.32
			0.428 (±0.023)	0.16
$K[Fe_{0.4}Mn_{0.6}]FeF_6$	0.72 (Fe^{3+})	0.42	0.358 (±0.006)	0.42
			0.337 (±0.006)	0.38
	—(Fe^{2+})		0.421 (±0.012)	0.08
			0.393 (±0.014)	0.12
	—(Fe^{2+})	—	Unresolved	—
			0.421 (±0.012)	0.08
	—(Fe^{2+})	—	Unresolved	—
			0.393 (±0.014)	0.12

[a] All values in mm-sec^{-1}.

[b] Relative to sodium nitroprusside.

[c] Lower velocity member listed first.

equal or are close to those predicted by the model of Buchanan *et al.*

The broader than normal linewidths observed for the Fe^{3+} and Fe^{2+} Mössbauer spectra are consistent with this interpretation. We have observed similar linewidths (*6*) in our studies of the modified pyrochlores $AM^{II}M^{III}F_6$ which have cubic structures in which the trivalent and divalent ions are distributed over the structurally equivalent 16(*c*) sites. Consideration of the tetragonal bronze structure (*2*) (the $Z = \frac{1}{2}$ plane is especially illustrative of this point) reveals that ions on the 8(*j*) sites have as nearest-neighbor multivalent cations ions on both 8(*j*) and 2(*c*) sites. The same is true for cations on the 2(*c*) sites. With both M^{3+} and M^{2+} ions distributed over the 8(*j*) sites and M^{2+} ions on the 2(*c*) sites one would not expect the local symmetry to be identical for all 8(*j*) sites (or for all 2(*c*) sites)

TABLE II
AREA RATIOS BETWEEN HIGHER VELOCITY COMPONENTS OF THE Fe^{2+} SPECTRA

$KM^{II}M^{III}F_6$	Area ratio
$KFeVF_6$	0.28/0.19 = 1.47
$KFeCrF_6$	0.25/0.18 = 1.40
$K[Fe_{0.4}Mg_{0.6}]VF_6$	0.25/0.20 = 1.25
$K[Fe_{0.4}Mn_{0.6}]CrF_6$	0.20/0.16 = 1.25
$K[Fe_{0.4}Mn_{0.6}]FeF_6$	0.12/0.08 = 1.50

even though we consider them structurally equivalent. We have a situation analogous to that occurring in the modified pyrochlores and this variation in local site symmetries is reflected in the broadened linewidths, and explains the slight asymmetry in the Fe^{3+} magnetic hyperfine pattern reported for $K_{0.4}FeF_3$ by Greenwood *et al.* without requiring that the Fe^{3+} ions be distributed on crystallographically nonequivalent sites.

In our study of fluorides having the "tetragonal bronze" structure we have prepared compositions for which the Mössbauer spectra clearly show the presence of two kinds of Fe^{2+}. The area ratios of these resolved absorptions provide a quantitative demonstration of the site distribution of Fe^{2+} in these materials which could only be inferred by Buchanan *et al.* from the very large linewidths observed for the Fe^{2+} absorption in $K_{0.5}FeF_3$. We have also shown that a careful analysis of the consequences of such a distribution of ions in the tetragonal structure explains not only the broadened linewidths observed but also removes the apparent discrepancy between the work of Buchanan *et al.* and Greenwood *et al.*

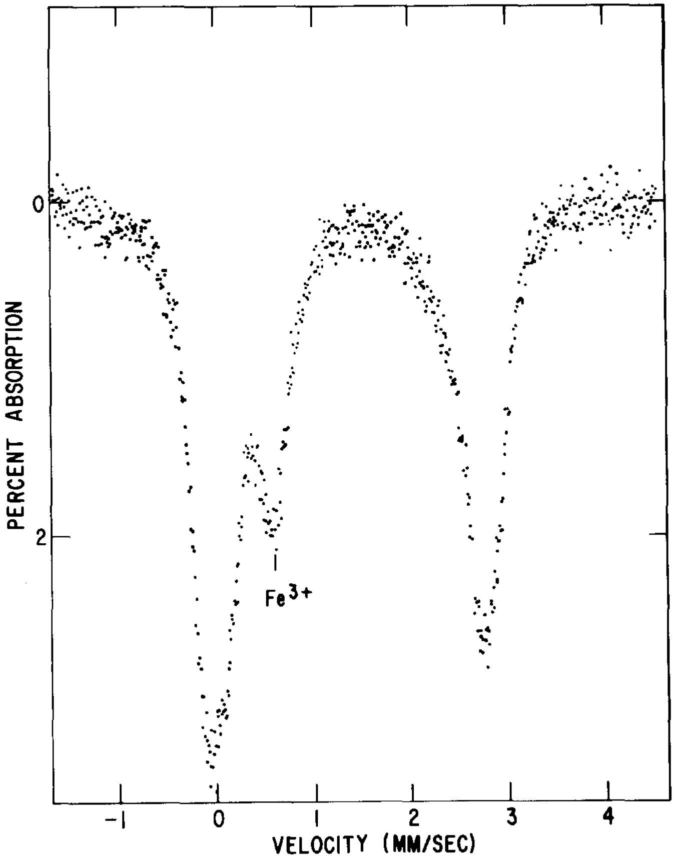

FIG. 2. The 77°K Fe^{57} Mössbauer spectrum of $K[Fe_{0.4}Mn_{0.6}]CrF_6$.

It should be noted that whereas a site preference does exist in the tetragonal bronze fluorides additional studies are required to determine if the mechanism of site preference is determined by the properties of the divalent or trivalent ions.

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