

Mössbauer Spectroscopy and Magnetic Properties of $\text{Ba}_5\text{Fe}_{3-x}^{\text{III}}\text{M}_x^{\text{II}}\text{F}_{19-x}$ ($M = \text{Fe}, \text{Cu}$)

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Received February 7, 1996; in revised form May 14, 1996; accepted May 16, 1996

The Mössbauer spectra of three phases of the tetragonal solid solution $\text{Ba}_5\text{Fe}_{3-x}^{\text{III}}\text{M}_x^{\text{II}}\text{F}_{19-x}$ ($M = \text{Fe}, \text{Cu}$) obtained by substitution of Fe^{3+} by M^{2+} ions, have been studied, as well as their magnetic properties. A mechanism of substitution of the Fe^{3+} cations is proposed according to the Mössbauer data. These compounds are paramagnetic until 4.2 K, with very weak antiferromagnetic interactions below 30–40 K. © 1996 Academic Press, Inc.

INTRODUCTION

$\text{Ba}_5\text{M}_3\text{F}_{19}$ fluorides, all tetragonal, are disclosed in many $\text{BaF}_2\text{--MF}_3$ binary systems ($M = \text{Cr}, \text{Fe}, \text{Ga}, \text{In}, \text{Al}$) (1–5). These compounds are the lower limit of solid solutions formulated $\text{Ba}_5\text{M}_{3-x}^{\text{III}}\text{M}'_x^{\text{II}}\text{F}_{19-x}$ with $0 \leq x \leq 1$, obtained by substitution of one third of the trivalent cations by bivalent cations. So, the upper limit of these solid solutions must be formulated $\text{Ba}_5\text{M}_2^{\text{III}}\text{M}'^{\text{II}}\text{F}_{18}$. In a previous work (6), we studied the ternary system $\text{BaF}_2\text{--ScF}_3\text{--CuF}_2$ and particularly the solid solution $\text{Ba}_5\text{Sc}_{3-x}\text{Cu}_x\text{F}_{19-x}$ with $0 \leq x \leq 1$. We showed that the cell parameters do not follow Vegard's law, implying that the substitution of Sc^{3+} by Cu^{2+} is ordered. This fact is corroborated by the apparition of superstructure lines on the X-ray powder pattern of $\text{Ba}_5\text{Sc}_2\text{CuF}_{18}$. We proposed a mechanism of substitution based on the description of the crystal structures of $\text{Pb}_5\text{Fe}_3\text{F}_{19}$ (7), $\text{Sr}_5\text{Fe}_3\text{F}_{19}$ (8), and $\text{Ba}_5\text{Cr}_2\text{CrF}_{18}$ (9). In the present work, we give some new arguments in favor of our mechanism hypothesis, by a Mössbauer spectroscopic study of the three phases: $\text{Ba}_5\text{Fe}_{2.8}^{\text{III}}\text{Fe}_{0.2}^{\text{II}}\text{F}_{18.8}$, $\text{Ba}_5\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{F}_{18}$, and

$\text{Ba}_5\text{Fe}_2^{\text{III}}\text{Cu}^{\text{II}}\text{F}_{18}$. These compounds are also characterized by X-ray diffraction and the thermal variation of their magnetic susceptibilities is measured.

SYNTHESES

The binary fluorides used in this work were prepared in the laboratory. To obtain iron(III) fluoride, first $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ is prepared in solution by reaction in a platinum crucible between $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (R. P. Normapur) and an excess of fluorhydric acid at 40% (R. P. Normapur); the liquid is evaporated at 60°C and the solid is then slowly dehydrated in 6 h into light green FeF_3 under an anhydrous hydrogen fluoride stream at 750°C.

Iron(II) fluoride is prepared starting from $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (R. P. Normapur). The chloride is first dehydrated into FeCl_2 under an anhydrous hydrogen chloride stream at 250°C in 3 h and then immediately fluorinated in the same reactor into light beige FeF_2 by anhydrous hydrogen fluoride at 650°C in 4 h.

The colorless copper fluoride CuF_2 is prepared by reaction between its hydroxycarbonate (Merck, extra pure) and anhydrous hydrogen fluoride at 500°C. It is slightly hygroscopic, must be protected from moisture in a dessicator, and used within 2 weeks.

The ternary and quaternary fluorides $\text{Ba}_5\text{Fe}_3\text{F}_{19}$ and $\text{Ba}_5\text{Fe}_2\text{MF}_{18}$ ($M = \text{Fe}, \text{Cu}$) are synthesized by solid state reaction at 790°C for 20 h, in sealed gold tubes, starting from stoichiometric mixtures of the binary fluorides.

X-RAY DIFFRACTION

The cell parameters (Table 1) are determined and refined from X-ray powder diffraction data collected on a

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TABLE 1
Refined Cell Parameters for $\text{Ba}_5\text{Fe}_{3-x}^{\text{III}}\text{M}_x^{\text{II}}\text{F}_{19-x}$ ($M = \text{Fe}, \text{Cu}$)

Compound	a (Å)	c (Å)	Z
$\text{Ba}_5\text{Fe}_{2.8}^{\text{III}}\text{Fe}_{0.2}^{\text{II}}\text{F}_{18.8}$	$a_{\text{F18.8}} = 14.664(1)$	$c_{\text{F18.8}} = 7.686(1)$	4
$\text{Ba}_5\text{Fe}_2\text{FeF}_{18}$	$a_{\text{F18.8}} \times \sqrt{2} \approx a_{\text{F18}}$ $= 20.565(2)$	$c_{\text{F18.8}} \times 2 \approx c_{\text{F18}}$ $= 15.347(2)$	16
$\text{Ba}_5\text{Fe}_2\text{CuF}_{18}$	$a_{\text{F18.8}} \times \sqrt{2} \approx a_{\text{F18}}$ $= 20.568(2)$	$c_{\text{F18.8}} \times 2 \approx c_{\text{F18}}$ $= 15.429(2)$	16

17 cm vertical Philips PW 1050/25 diffractometer using a copper anticathode ($\lambda = 1.5418$ Å). The diffraction patterns are analyzed by the program EVA 3.01 (SOCABIM) which allows the deconvolution of the $K\alpha_2$ component and the determination of the peak positions. According to the Mössbauer results, a part of the Fe^{3+} ions was reduced into Fe^{2+} during the synthesis of $\text{Ba}_5\text{Fe}_3\text{F}_{19}$. So, the compound prepared must be formulated $\text{Ba}_5\text{Fe}_{2.8}^{\text{III}}\text{Fe}_{0.2}^{\text{II}}\text{F}_{18.8}$. All these fluorides (Tables 2–4) are indexed in the tetragonal system, using the crystal structure data of $\text{Ba}_5\text{Fe}_3\text{F}_{19}$ (10) for $\text{Ba}_5\text{Fe}_{2.8}^{\text{III}}\text{Fe}_{0.2}^{\text{II}}\text{F}_{18.8}$ and by isotypy with $\text{Ba}_5\text{Cr}_2\text{CrF}_{18}$ (9) for the two other phases.

DESCRIPTION OF THE STRUCTURE OF $\text{Ba}_5\text{Fe}_3\text{F}_{19}$ AND OF THE $\text{Ba}_5\text{Cr}_2\text{CrF}_{18}$ -TYPE COMPOUNDS

The structures of $\text{Ba}_5\text{Fe}_3\text{F}_{19}$ (10) and $\text{Ba}_5\text{Cr}_2\text{CrF}_{18}$ (9) have been described by Welsch and Babel. They are closely related and based on three subnetworks (Table 5): isolated $[\text{MF}_6]$ octahedra which form two kinds of channels along the c axis (Fig. 1). The first channels contain isolated dimers $[\text{M}_2\text{F}_{10}]$ (Fig. 2) and in the second channels are inserted “independent” fluorine ions which form with barium ions infinite chains of edge-sharing or vertex-sharing $[\text{FBa}_4]$ tetrahedra.

TABLE 2
 d Spacings (Å) in $\text{Ba}_5\text{Fe}_{2.8}^{\text{III}}\text{Fe}_{0.2}^{\text{II}}\text{F}_{18.8}$

$d_{\text{mes.}}$	$d_{\text{calc.}}$	$h k l$	l/I_0	$d_{\text{mes.}}$	$d_{\text{calc.}}$	$h k l$	l/I_0
7.31	7.332	2 0 0	4	2.567	2.567	5 2 1	6
5.18	5.184	2 2 0	4	2.515	2.515	5 3 0	2
4.98	4.989	2 1 1	3	2.444	2.444	6 0 0	9
4.63	4.637	3 1 0	6	2.386	2.386	2 1 3	10
3.841	3.843	0 0 2	40	2.319	2.319	6 2 0	15
3.664	3.666	4 0 0	18	2.303	2.303	5 1 2	19
3.593	3.595	3 2 1	55	2.195	2.195	5 4 1	9
3.453	3.456	3 3 0	13	2.168	2.168	3 2 3	20
3.402	3.404	2 0 2	53	2.149	2.149	4 4 2	2
3.278	3.279	4 2 0	50	2.104	2.104	5 3 2	34
3.226	3.228	4 1 1	100	2.079	2.079	4 1 3	47
3.086	3.087	2 2 2	55	2.062	2.062	6 0 2	18
2.876	2.876	5 1 0	2	1.949	1.949	7 2 1	3

TABLE 3
 d Spacings (Å) in $\text{Ba}_5\text{Fe}_2\text{FeF}_{18}$

$d_{\text{mes.}}$	$d_{\text{calc.}}$	$h k l$	l/I_0	$d_{\text{mes.}}$	$d_{\text{calc.}}$	$h k l$	l/I_0
7.26	7.271	2 2 0	6	3.425	3.427	6 0 0	14
6.15	6.150	2 0 2	1	3.393	3.393	2 2 4	35
5.34	5.346	3 2 1	3	3.250	3.252	6 2 0	35
5.14	5.141	4 0 0	4	3.203	3.205	5 3 2	100
4.95	4.961	3 1 2	2	3.075	3.075	4 0 4	37
4.60	4.599	4 2 0	7	2.547	2.547	7 3 2	6
4.46	4.471	2 1 3	1	2.515	2.516	7 4 1	3
4.096	4.098	3 3 2	2	2.482	2.481	6 2 4	4
3.941	3.944	4 2 2	2	2.425	2.424	6 6 0	3
3.835	3.837	0 0 4	25	2.380	2.380	3 1 6	8
3.705	3.710	1 1 4	3	2.299	2.299	8 4 0	27
3.633	3.635	4 4 0	10	2.289	2.289	6 4 4	21
3.568	3.570	5 1 2	74	2.235	2.235	4 2 6	3

This structural description of the “F19” and “F18” type compounds shows that the substitution of M^{3+} by M^{2+} in $\text{Ba}_5\text{M}_3\text{F}_{19}$ must be ordered. This fact is corroborated by the apparition of superstructure lines on the X-ray powder patterns of the $\text{Ba}_5\text{Fe}_2\text{MF}_{18}$ compounds ($M = \text{Fe}^{2+}, \text{Cu}^{2+}$) (for example: 3 2 1 at 5.34 Å on the pattern of $\text{Ba}_5\text{Fe}_2\text{FeF}_{18}$), implying a larger cell compared with that of $\text{Ba}_5\text{Fe}_3\text{F}_{19}$ (10). The substitution of Fe^{3+} by M^{2+} takes place in the first channels, i.e., in the dimers, and the centers of the barium tetrahedra inserted in the second type of channels are all occupied by independent fluorine ions for “F19” and only half of them for “F18”.

MÖSSBAUER SPECTROSCOPY OF $\text{Ba}_5\text{Fe}_{2.8}^{\text{III}}\text{Fe}_{0.2}^{\text{II}}\text{F}_{18.8}$ AND $\text{Ba}_5\text{Fe}_2^{\text{III}}\text{M}^{\text{II}}\text{F}_{18}$ ($M = \text{Fe}, \text{Cu}$)

The Mössbauer spectra of samples containing 5 mg/cm² of natural iron were recorded at 300, 77, and 4.2 K using

TABLE 4
 d Spacings (Å) in $\text{Ba}_5\text{Fe}_2\text{CuF}_{18}$

$d_{\text{mes.}}$	$d_{\text{calc.}}$	$h k l$	l/I_0	$d_{\text{mes.}}$	$d_{\text{calc.}}$	$h k l$	l/I_0
7.27	7.272	2 2 0	7	2.488	2.486	6 2 4	2
5.14	5.142	4 0 0	4	2.391	2.391	3 1 6	8
4.97	4.973	3 1 2	3	2.343	2.344	6 5 3	2
4.60	4.599	4 2 0	8	2.294	2.293	6 4 4	23
3.854	3.857	0 0 4	34	2.179	2.179	9 1 2	11
3.635	3.636	4 4 0	15	2.169	2.168	5 1 6	19
3.574	3.574	5 1 2	56	2.139	2.139	8 0 4	3
3.428	3.428	6 0 0	16	2.093	2.094	8 2 4	18
3.406	3.407	2 2 4	49	2.087	2.087	9 3 2	29
3.251	3.252	6 2 0	45	2.078	2.078	5 3 6	41
3.208	3.208	5 3 2	100	2.057	2.057	8 6 0	20
3.084	3.086	4 0 4	66	1.976	1.975	8 4 4	2
2.562	2.562	6 0 4	2	1.929	1.929	0 0 8	18
2.549	2.549	7 3 2	3	1.863	1.862	7 3 6	2

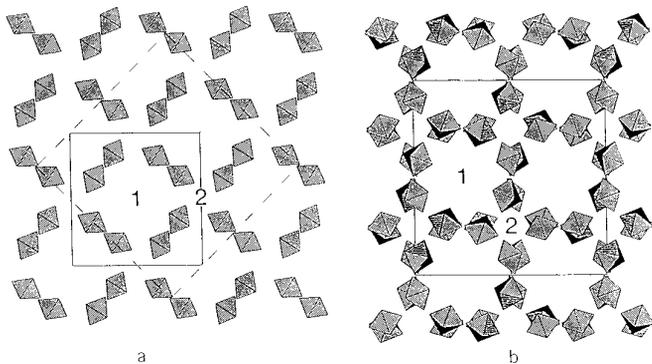


FIG. 1. (001) projection of the $[M_2F_{12}]$ subnetwork in $Ba_5Fe_3F_{19}$ (a) and $Ba_5Cr_2CrF_{18}$ (b). 1 and 2 indicate the two kinds of channels.

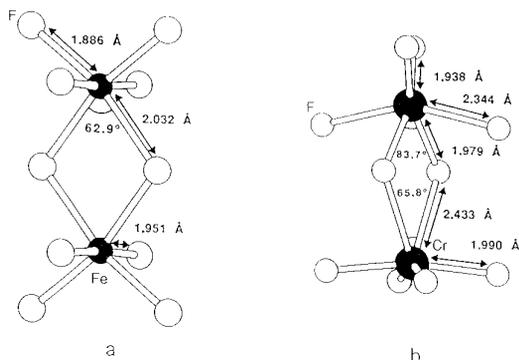


FIG. 2. $[M_2F_{10}]$ dimers in $Ba_5Fe_3F_{19}$ (a) and $Ba_5Cr_2CrF_{18}$ (b).

a ^{57}Co radioactive source diffused in a rhodium matrix. The spectra recorded at 4.2 K are similar to those obtained at 77 K: they are therefore not described hereafter.

The isomer shift relative to metallic iron (I.S.) and the

TABLE 5
Comparison of the Three Subnetworks
in $Ba_5Fe_3F_{19}$ and $Ba_5Cr_2CrF_{18}$

Subnetwork	$Ba_5Fe_3F_{19}$ ($I4/m$)	$Ba_5Cr_2CrF_{18}$ ($I4_1/a$)
$[M_2F_{12}]$	Isolated $[M^{III}F_6]^{3-}$ octahedra (Fig. 1)	
$[MF_5]$	Isolated dimers $[Fe_2^{III}F_{10}]^{4-}$ of two octahedra (Fig. 2a)	Isolated dimers $[Cr_2^{II}F_{10}]^{6-}$ of octahedron + prism (Fig. 2b)
$[Ba_5F_2]$ or $[Ba_5F]$	Infinite chains of edge-sharing $[FBa_4]$ tetrahedra	Twisted chains of vertex-sharing $[FBa_4]$ tetrahedra

quadrupolar splitting (Q.S.) (Table 6) are in agreement with the usual observed values for iron(II) and iron(III) six-coordinated in high-spin fluorides (11). Nevertheless, the Lorentzian linewidths (Γ) are large, specially for the iron(III) which exhibits a linewidth Γ double in comparison with the natural one. This anomalous line broadening, already observed for other compounds with isolated iron polyhedra, can be attributed to an electronic relaxation effect (12).



The spectra recorded at 300 and 77 K exhibit a well resolved quadrupolar doublet and a single line of weak intensity (Fig. 3). This one is in agreement with a parasitic iron(II) component ($\approx 6\%$ rate of the total iron at 300 K). At 4.2 K the compound is always paramagnetic despite a strong broadening of the linewidth of the doublet which

TABLE 6
Mössbauer Data for $Ba_5Fe_{2.8}^{III}Fe_{0.2}^{II}F_{18.8}$ and $Ba_5Fe_2^{III}M^{II}F_{18}$ ($M = Fe, Cu$)

Compound	Fe ^{III}						Fe ^{II}				
	T (K)	I.S. ^a	Γ (mm/s) ± 0.01	Q.S.	% ± 2	% Fe ^{III}	I.S. ^a	Γ (mm/s) ± 0.01	Q.S.	% ± 2	% Fe ^{II}
$Ba_5Fe_{2.8}^{III}Fe_{0.2}^{II}F_{18.8}$	300	0.43	0.40	0.35	67						
		0.43	0.40	0.67	27	94	1.09	0.32	2.23	6	6
	77	0.49	0.42	0.40	71						
		0.49	0.42	0.85	20	91	1.66	0.36	2.40	9	9
$Ba_5Fe_2CuF_{18}$	300	0.41	0.54	0.33	100	100					
	77	0.52	0.48	0.38	100	100					
$Ba_5Fe_2FeF_{18}$	300	0.43	0.47	0.33	63	63	1.24	0.36	1.45	19	
								1.23	0.33	2.46	18
	77	0.53	0.45	0.32	63	63	1.39	0.32	1.62	15	
								1.36	0.35	2.56	22

^a Isomer shift relative to metallic iron at 300 K.

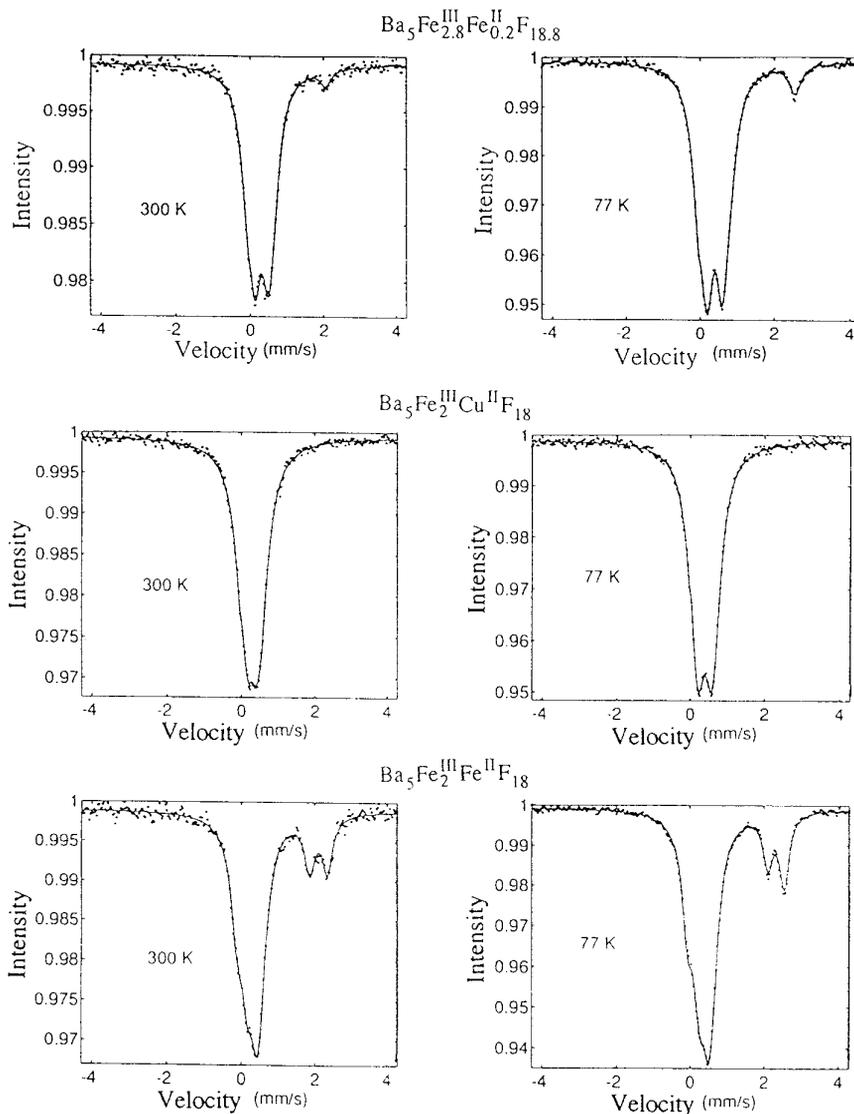


FIG. 3. Mössbauer spectra at 300 and 77 K for $\text{Ba}_5\text{Fe}_{2.8}^{\text{III}}\text{Fe}_{0.2}^{\text{II}}\text{F}_{18.8}$, $\text{Ba}_5\text{Fe}_2\text{CuF}_{18}$, and $\text{Ba}_5\text{Fe}_2\text{FeF}_{18}$.

indicates a beginning of a tridimensional magnetic order. The Fe^{2+} component is still in a paramagnetic state at this temperature, indicating that the Fe^{2+} cations are well part of the structure. So, the latter must be formulated $\text{Ba}_5\text{Fe}_{3-x}^{\text{III}}\text{Fe}_x^{\text{II}}\text{F}_{19-x}$ with $x \sim 0.18$. The theoretical distribution of the Fe^{3+} cations in $\text{Ba}_5\text{Fe}_3\text{F}_{19}$ (space group $I4/m$, No. 87 (10)) is 67% in the isolated octahedra (site $8h$) and 33% in the isolated dimer (site $4e$). The fitted results given in Table 6 indicate the presence of two Fe^{3+} sites with, at 300 K,

Site 1	Q.S. = 0.35 mm/s	$P = 67\%$
Site 2	Q.S. = 0.67 mm/s	$P = 27\%$.

Site 1 corresponds to the isolated, quite regular, octahe-

dra, with a local symmetry of the octahedron which leads to a Q.S. value of 0.35 mm/s. Site 2 corresponds to the isolated dimer and the 6% rate of Fe^{2+} cations only takes place in the dimer: $27 + 6 = 33\%$.

$\text{Ba}_5\text{Fe}_2^{\text{III}}\text{Cu}^{\text{II}}\text{F}_{18}$

In this compound, isostructural with $\text{Ba}_5\text{Cr}_2\text{CrF}_{18}$ (space group $I4_1/a$, No. 88 (9)), exist four potential independent crystallographic sites for iron(III): two independent and quite regular octahedral sites in the $[\text{M}_2\text{F}_{12}]$ subnetwork (sites $16f$) and two distorted six-coordinated sites in the $[\text{M}_2\text{F}_{10}]$ dimer (sites $8e$). On the Mössbauer spectra only one single Fe^{3+} component is observed, leading to a fitted Q.S. value of 0.33 mm/s at 300 K (Fig. 3). In agreement with the results observed for the Q.S. in

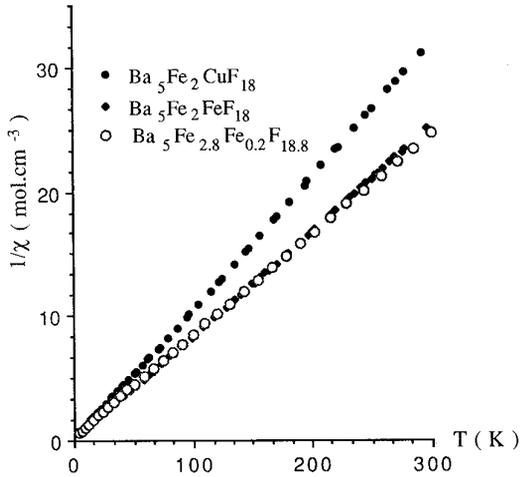


FIG. 4. Thermal variation of the reciprocal molar susceptibilities for $\text{Ba}_5\text{Fe}_{2.8}^{III}\text{Fe}_{0.2}^{II}\text{F}_{18.8}$ and $\text{Ba}_5\text{Fe}_2^{III}M^{II}\text{F}_{18}$ ($M = \text{Fe}, \text{Cu}$).

$\text{Ba}_5\text{Fe}_{2.8}^{III}\text{Fe}_{0.2}^{II}\text{F}_{18.8}$, the Fe^{3+} ions may only occupy the regular octahedral sites of the $[\text{M}_2\text{F}_{12}]$ subnetwork. The Cu^{2+} ions are then all localized in the dimer.

$\text{Ba}_5\text{Fe}_2^{III}\text{Fe}^{II}\text{F}_{18}$

In this compound, isostructural with $\text{Ba}_5\text{Fe}_2\text{CuF}_{18}$, one single Fe^{3+} component and two distinct Fe^{2+} components are observed on the Mössbauer spectra (Fig. 3). The fitted data lead to a Q.S. for the Fe^{3+} cations of 0.33 mm/s, in agreement with a location of the latter in the regular octahedral sites of the $[\text{M}_2\text{F}_{12}]$ subnetwork. The Fe^{3+} rate is near 2/3 of the total iron.

The remaining 1/3 of the total iron which corresponds to the Fe^{2+} ions is localized in the isolated dimers. The local symmetries of the two sites of the dimer are not equivalent. This fact is well demonstrated by the Fe^{2+} ions which amplify the local symmetry effect (13), with two very different values for the quadrupolar splitting. The occupation rate of the two sites is equal (50/50), in agreement with a dimeric entity.

MAGNETIC MEASUREMENTS ON $\text{Ba}_5\text{Fe}_{2.8}^{III}\text{Fe}_{0.2}^{II}\text{F}_{18.8}$ AND $\text{Ba}_5\text{Fe}_2^{III}M^{II}\text{F}_{18}$ ($M = \text{Fe}, \text{Cu}$)

Magnetic measurements were carried out between 4.2 and 300 K by the Faraday method with $H_{\text{max}} = 10000$ G. The powder samples were inserted into an air-tight Teflon container and diamagnetic corrections were applied. The plots of the reciprocal molar susceptibility χ_M^{-1} versus temperature for the three compounds are displayed in Fig. 4. Above 30–40 K, Curie–Weiss laws are well obeyed with Curie constants C_M and paramagnetic Curie temperatures

TABLE 7
Curie Constants C_M and Paramagnetic Curie Temperatures θ_p for $\text{Ba}_5\text{Fe}_{2.8}^{III}\text{Fe}_{0.2}^{II}\text{F}_{18.8}$ and $\text{Ba}_5\text{Fe}_2^{III}M^{II}\text{F}_{18}$ ($M = \text{Fe}, \text{Cu}$)

Compounds	$C_{M(\text{obs.})}$ ($\text{mol}^{-1} \cdot \text{cm}^3 \cdot \text{K}$)	$C_{M(\text{th.})}$ ($\text{mol}^{-1} \cdot \text{cm}^3 \cdot \text{K}$)	θ_p (K)
$\text{Ba}_5\text{Fe}_{2.8}^{III}\text{Fe}_{0.2}^{II}\text{F}_{18.8}$	12.46	12.85	-6.7
$\text{Ba}_5\text{Fe}_2\text{CuF}_{18}$	9.33	9.13	+1.9
$\text{Ba}_5\text{Fe}_2\text{FeF}_{18}$	11.90	11.75	+0.3

θ_p given in Table 7. The Curie constants are very close to the theoretical ones calculated with the usual Curie constants for Fe^{3+} and Cu^{2+} and for the Fe^{2+} cation with a locked orbital moment. Below about 40 K, the decrease of $\chi \cdot T$ may indicate weak antiferromagnetic interactions (Fig. 5). Nevertheless, the greatest care must be taken for more precise interpretations, because θ_p values and interactions are very weak. According to the structure of these compounds, direct exchanges between transition ions are impossible. However, indirect exchanges through one F^- ion between two transition ions, M^{3+} in $\text{Ba}_5\text{Fe}_3\text{F}_{19}$ and M^{2+} in $\text{Ba}_5\text{Fe}_2M\text{F}_{18}$ ($M = \text{Cu}^{2+}, \text{Fe}^{2+}$), can occur in the dimers, as well as weak long-range interactions through F^- anions. In any case, the absence of a Zeeman sextet in the Mössbauer spectra between 40 and 4.2 K rules out the possibility of a 3-D cooperative extension of these interactions above 4.2 K. Only a line broadening is observed on the spectra, which confirms a beginning of a tridimensional magnetic order in agreement with the magnetic measurements. The Néel temperature of all these fluorides must be considerably lower than 4.2 K.

CONCLUSION

Mössbauer spectroscopy has demonstrated that the substitution of Fe^{3+} by Fe^{2+} or Cu^{2+} cations in $\text{Ba}_5\text{Fe}_3\text{F}_{19}$ to

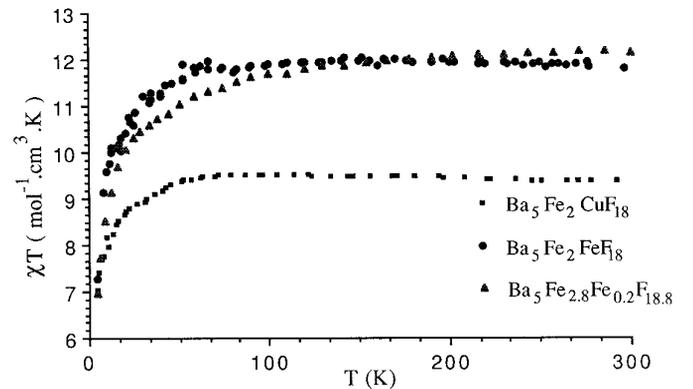


FIG. 5. Thermal variation of $\chi \cdot T$ for $\text{Ba}_5\text{Fe}_{2.8}^{III}\text{Fe}_{0.2}^{II}\text{F}_{18.8}$ and $\text{Ba}_5\text{Fe}_2^{III}M^{II}\text{F}_{18}$ ($M = \text{Fe}, \text{Cu}$).

give $\text{Ba}_5\text{Fe}_{3-x}^{\text{III}}\text{M}'_x^{\text{II}}\text{F}_{19-x}$ is strictly ordered and only takes place in the dimers. Therefore it is not possible to substitute more than one third of the Fe^{3+} cations of the structure: x is limited to the value 1. This limit is also observed for the solid solution $\text{Ba}_5\text{Sc}_{3-x}\text{Cu}_x\text{F}_{19-x}$ (6) and for all the other $\text{Ba}_5\text{M}'_{3-x}\text{M}''_x\text{F}_{19-x}$ solid solutions hitherto described ($M = \text{Cr, Fe, V, Ga}$; $M' = \text{Ni, Mn, Cu, Fe}$) (1–3, 14–17).

The three compounds $\text{Ba}_5\text{Fe}_{2.8}^{\text{III}}\text{Fe}_{0.2}^{\text{II}}\text{F}_{18.8}$, $\text{Ba}_5\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{F}_{18}$, and $\text{Ba}_5\text{Fe}_2^{\text{III}}\text{Cu}^{\text{II}}\text{F}_{18}$ are paramagnetic until 4.2 K. However, weak and localized antiferromagnetic interactions occur below 30–40 K. The broadening of the linewidth of the Fe^{3+} Mössbauer doublets in $\text{Ba}_5\text{Fe}_{2.8}^{\text{III}}\text{Fe}_{0.2}^{\text{II}}\text{F}_{18.8}$ at 4.2 K indicates a beginning of a tridimensional magnetic order. Some new measurements are in progress, especially to determine the Néel temperatures of these compounds.

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