Magnetic Properties of the Dimeric Iron(III) Fluoride: $Cs_3Fe_2F_9$

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The crystal structure of $Cs_3Fe_2F_9$ has been redetermined with more accuracy. It consists of binuclear entities of face-sharing octahedra containing iron(III). The magnetic properties have been analyzed on the basis of ferromagnetic interactions within the isolated units, which are unusual for d^5 ions. However, at low temperature intercoupling between dimers arise and has to be taken into account to fit the susceptibility data in the considered temperature range. © 1986 Academic Press, Inc.

Introduction

Polynuclear magnetic entities have been recently studied in the particular case of the hexagonal perovskite type series of fluorides and oxide fluorides (*1–3*). Binuclear entities may exist in the 2H-hexagonal structure, consisting of infinite chains of face-sharing octahedra, if one third of the octahedra is vacant as it appears for $Cs_3V_2O_2F_7$ (*4*) or $Cs_3Fe_2F_9$ (*5*).

The original determination of the $Cs_3Fe_2F_9$ structure was based on film intensities (*5*). A redetermination using diffractometer data seemed desirable before investigating the magnetic properties of the binuclear compound and proposing an interpretation of them. In addition to the demand for more accurate interatomic distances, the question of the true space group arose, because in the meantime some possibly isostructural phases such as $Cs_3V_2O_2F_7$

$(4, 6)$ and $Cs_3Mo_2O_6F_3$ $(6, 7)$ were successfully refined in the higher symmetry space group: $P6_3/mmc$. This paper reports a more precise determination of the structure and the analysis of the magnetic properties of $Cs_3Fe_2F_9$.

I. Synthesis and Crystal Structure

By heating a $3\ CsF + 2\ FeF_3$ mixture in a sealed platinum tube for 2 days at 700°C and subsequent slow cooling a crystalline material was obtained, from which a single crystal of about $0.50 \times 0.24 \times 0.10\ mm^3$ dimensions was selected for X-ray examination. Using an automatic four-circle diffractometer CAD4 (ENRAF-NONIUS) the lattice constants quoted in Table I were determined and intensity data collected and evaluated as given in Table I. The reliability indices achieved in space group $P6_3/mmc$ allowed to discard the former assignment of

$P\bar{6}2c$ (5). Some violations of the only systematic absences (*hhl*: $l \neq 2n$) were undoubtedly due to Renninger effect (8), as checked by repeated measurements at different ψ settings.

Table II gives the atomic parameters and Table III the resulting atomic distances for the redetermined $Cs_3Fe_2F_9$ structure. A list of structure factors has been deposited.[1]

The standard deviations of the new values in the centrosymmetric space group $P6_3/mmc$ are about 10 times better than those obtained with the previous acentric choice (5). But neglecting the higher symmetry and accuracy obtained now, the average distances of the former determination

[1] Obtainable from Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, under specification of deposit No. CSD51608, authors and journal reference.

could be essentially confirmed, so as to make a new discussion unnecessary. However, the largest change observed is at the same time the most important one and refers to the Fe–Fe distance in the binuclear unit illustrated in Fig. 1: the new value of 291.6 pm is significantly shorter than previously reported (294.8 pm) (5). In the isostructural oxide fluorides already mentioned the higher charge of the M cations leads to larger M–M separations (4, 7).

II. Magnetic Properties

The magnetic data of $Cs_3Fe_2F_9$ have been determined in the temperature range 1.7–300 K using both a SQUID S.H.E. magnetometer and a Faraday balance. After correcting for diamagnetic contribution the susceptibility follows a Curie–Weiss law at

TABLE I

$Cs_3Fe_2F_9$ Crystal Data and Conditions of Measurements and Evaluation

Lattice constants (pm)	$a = 634.7(1)$ (634.5 (Ref. 5))
	$c = 1480.5(3)$ (1481.6 (Ref. 5))
Space group	$P6_3/mmc$, $Z = 2$
Molecular mass	681.39
Density (g cm^{-3})	$d_c = 4.379$, $d_0 = 4.33$
Radiation	$MoK\alpha$, graphite monochromatized
Scanning mode and aperture	ω $(1.1 + 0.35$ tg $\theta)°$
Measuring time per reflection	45 s max.
θ range measured (°)	2/32
h, k, l min/max	0/9, $-9/9$, $-22/22$
Total of reflections measured	3200
Independent reflections	386
Used in Refinement	379 with $F_0 > 4\sigma(F_0)$
Absorption	$\mu = 126.1$ cm^{-1}, numerically corrected
Transmission factors min/max	0.07/0.29
Computer	TR 440, Rechenzentrum der Universität Marburg
Atomic form factors	Neutral atoms (9), corrected for anomalous dispersion (10)
Programs used	STRUX (11), SHELX (12), ORTEP (13)
Weights refined	$k = 20.5$ in $w = k/\sigma^2(F_0)$
Extinction correction refined	$\varepsilon = 0.446 \times 10^{-6}$ in F_c(corr.) = $F_c(1 - \varepsilon F_c^2/\sin \theta)$
$R = \Sigma D/\Sigma |F_0|(D \equiv ||F_0| - |F_c||)$	0.0262
$R_w = \Sigma \sqrt{w}D/\Sigma \sqrt{w}|F_0|$	0.0202
$R_g = (\Sigma wD^2/wF_0^2)^{1/2}$	0.0242

TABLE II

REDUCED COORDINATES IN $Cs_3Fe_2F_9$, SPACE GROUP $P6_3/mmc$

Atom	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs1	(2d)	1/3	2/3	3/4	157(2)	U_{11}	194(2)	0	0	$U_{11}/2$
Cs2	(4f)	1/3	2/3	0.43271(3)	192(2)	U_{11}	294(2)	0	0	$U_{11}/2$
Fe	(4e)	0	0	0.15153(5)	134(2)	U_{11}	149(3)	0	0	$U_{11}/2$
F1	(6h)	0.1312(2)	2x	1/4	188(9)	121(11)	218(13)	0	0	$U_{22}/2$
F2	(12k)	0.1494(2)	2x	0.5940(1)	259(8)	165(9)	229(10)	52(7)	$U_{23}/2$	$U_{22}/2$

Note. The standard deviations (in parentheses) refer to the last digit(s). The anisotropic temperature factors U_{ij} in the expression $\exp[-2\pi^2(U_{11}h^2a^2 + \ldots + 2U_{12}hka^*b^*)]$ are given in units of $10^{-24}\ m^2$.

high temperature ($T > 15$ K) with $\theta_p = +3$ K and $C = 8.9$ ($C_{theor.} = 8.75$ for $Cs_3Fe_2F_9$) (Fig. 2). The positive value of θ_p supposes prevailing ferromagnetic interactions. At very low temperature (1.7 $< T <$ 6 K) (Fig. 2) the reciprocal susceptibility varies linearly with temperature with a Curie constant of 14.2. Such a magnetic behavior is characteristic of a ferromagnetic exchange within the magnetic isolated units.

The ground term of a Fe^{3+} ion is $^6A_{1g}$ in an octahedral surrounding. Therefore the exchange energy can be described using the Heisenberg–Dirac–Van Vleck Hamiltonian:

$$\mathcal{H}_{exch.} = -2J\mathbf{s}_1 \cdot \mathbf{s}_2$$

where J is the exchange interaction between nearest neighbor ions, and $\mathbf{s}_i$ ($i = 1$, 2), the spin operator associated with ion i. By vectorial decomposition of the angular

moments the eigenvalues $E_{(s)}$ of $\mathcal{H}_{exch.}$ can be obtained:

$$E_{(s)} = -J[S(S + 1)],$$

where S is the quantum number associated with the operator $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$.

The thermal dependence of the magnetic susceptibility can be obtained from a Van Vleck formulation:

$$\chi_{dimer.} = \frac{2Ng^2\beta^2}{kT}\{[55 + 30\exp(10x)$$

$$+ 14\exp(18x) + 5\exp(24x) + \exp(28x)]/[11$$

$$+ 9\exp(10x) + 7\exp(18x) + 5\exp(24x)$$

$$+ 3\exp(28x) + \exp(30x)]\} \quad (1)$$

with $x = -J/kT$.

TABLE III

INTERATOMIC DISTANCES (pm) AND ANGLES (°) IN $Cs_3Fe_2F_9$

Fe–F1	3×	205.1 bridg.	Fe–Fe		291.6
–F2	3×	185.0 term.	Fe–F1–Fe		90.6
–F	av.	195.1			
F1–F1		249.8	F1–Fe–F1		75.0
–F2		278.3/385.4	–Fe–F2		90.9/162.1
F2–F2		284.6	F2–Fe–F2		100.5
			Cs2–F1	3×	350.1
Cs1–F1*	6×	319.7	–F2	3×	312.9
–F2	6×	306.9	–F2*	6×	320.4
–F	av.	313.3	–F	av.	326.0

Note. Standard deviations are no larger than 0.3 pm and 0.1°. The asterisks refer to distances at about the same z height.
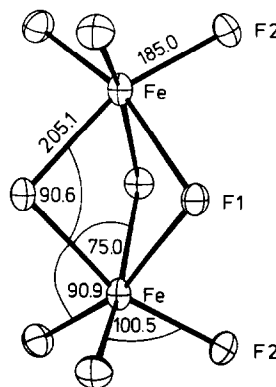

FIG. 1. The binuclear Fe_2F_9 unit in $Cs_3Fe_2F_9$ with Fe–Fe = 291.6 pm. The thermal ellipsoids correspond to a 50% probability level (13).
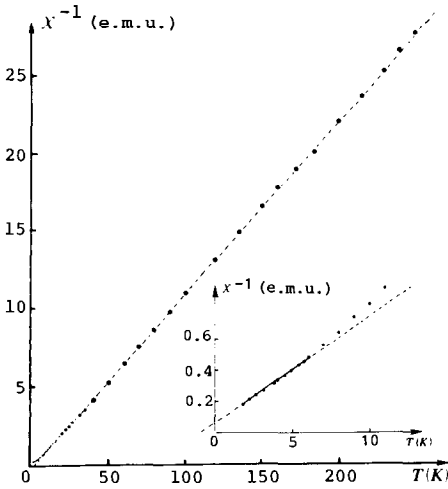
FIG. 2. Thermal variation of the reciprocal susceptibility of $Cs_3Fe_2F_9$.

An approximate value of the exchange integral can be obtained from the Weiss constant $\theta_p = +3.0$ K. In the χ_M expression, each exponential term can be substituted in first approximation by a power series of the form $\exp(x) \simeq 1 + x$.

It follows that

$$\chi_{dimer} = \frac{2Ng^2\beta^2}{kT} \frac{105 + 700x}{36 + 450x}$$

$$\simeq \frac{Ng^2\beta^2}{kT} \frac{2205}{378 + 2205x}.$$

Taking $g = 2$:

$$\chi_{dimer} = \frac{2205}{T(252 + 1470x)} = \frac{8.75}{T - \frac{35}{6} J/k}$$

$$= \frac{C}{T - \theta_p}.$$

Therefore the relation between θ_p and J/k is $\theta_p \simeq \frac{35}{6} J/k$ and the experimental value of $\theta_p = 3$ K corresponds to a J/k value of about $+0.5$ K.

The experimental data have been least-square fitted to the complete expression (1). The best agreement between calculated and observed values has been obtained for $J/k = +0.35$ K (with $g = 2$).

However, at very low temperatures the agreement between theory and experiment is no longer satisfactory. Experimental values of $\chi \cdot T$ decrease instead of reaching the expected finite upper value, for $T \rightarrow 0$ $\chi \cdot T = 15$, which results from the theoretical susceptibility for isolated ferromagnetic dimers (ground state $S = 5$) and Curie constant $C = 15$. A Curie–Weiss law is actually observed ($\theta_p = -1$ K) showing thus that intercoupling between dimers is negative.

One can deduce from this result that relatively strong intercluster effects occur between entities with weak ferromagnetic intracluster exchange. These clusters, in their spin aligned states, couple collectively at low temperature and thus modify the form of the corresponding susceptibility curve (1, 2, 14, 15). To include the intercluster exchange the term $-2z'J'\mathbf{S}_i \cdot \mathbf{S}_j$ has been added into the Hamiltonian, where J' is the effective intercluster exchange integral, z' the cluster lattice coordination number, $\mathbf{S}_i$ and $\mathbf{S}_j$ being, respectively, the total spin of clusters i and j. The correction for intercluster exchange has been derived in the molecular field approximation which allows to write (16)

$$\mathbf{S}_i \cdot \mathbf{S}_j = S_{iz}\langle S_{jz}\rangle.$$

The Hamiltonian including intercluster exchange becomes therefore

$$\mathcal{H}_{exch.} = -2J\mathbf{s}_i \cdot \mathbf{s}_2 - g\beta HS_z - 2z'J'S_z\langle S_z\rangle.$$

The eigenvalues of $\mathcal{H}_{exch.}$ may be written as

$$E(S, M_s) = E_0(S, M_s) - g\beta HM_s$$
$$- 2z'J'M_s\langle S_z\rangle$$

where $E_0(S, M_s)$ are the eigenvalues of $-2J\mathbf{s}_i \cdot \mathbf{s}_j$ in a zero field.

The susceptibility equation follows as

$$\chi = Ng^2\beta^2F(J, T)/(kT$$
$$- 2z'J'F(J, T))$$

with

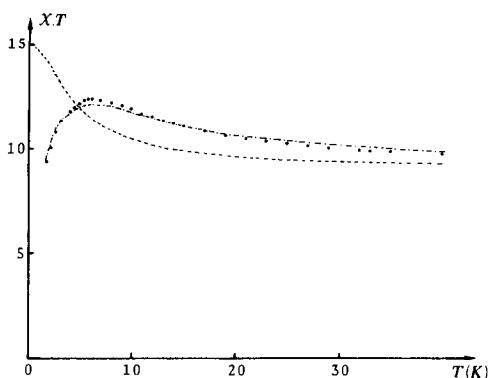$$F(J, T) = \sum_s \sum_{M_s} M_s^2 e^{-E_0(S,M_s)/kT}$$

FIG. 3. Dependence of the product $\chi \cdot T$ on temperature (the dashed curve is calculated with $J/k = +0.35_1$ K and $z'J''/k = 0$; the dotted-dashed curve is calculated with $J/k = +0.98_3$ K and $z'J''/k = -0.04_8$ K).

The best agreement between calculated and observed values has been obtained for $J/k = +0.98$ K and $z'J''/k = -0.04_8$ K (with $g = 2$) (Fig. 3).

To illustrate the contribution of the inter-cluster coupling on the magnetic behavior, the best least-square fitted parameters for the susceptibility at $T = 1.7$ K are given in Table IV. Mössbauer experiments indicate that the onset of a 3-D magnetic ordering occurs at least below 1.8 K (17) (Fig. 4). At 4.2 K the values of the quadrupole splitting $\overline{\Delta}$ and the isomer shift $\overline{\delta}$ are, respectively, $\overline{\Delta}$ = 0.55 mm/sec and $\overline{\delta}$ = 0.38 mm/sec. These values are characteristic of Fe(III) in octa-hedral environment. The positive value of the exchange interaction J/k results from prevailing ferromagnetic double-exchange correlations e_g-$p\sigma$-$p\sigma'$-e'_g between Fe^{3+} ions located in the face-sharing octahedra. Similar couplings have been observed in pairs of Ni^{2+} ions (d^8–d^8 interactions) (1, 2, 18).

FIG. 4. Mössbauer spectra of $Cs_3Fe_2F_9$.

However, the value of the exchange interaction for $Cs_3Fe_2F_9$ is here significantly lower despite shorter Fe–Fe distance within the $|Fe_2F_9|$ unit ($d = 2.91_6$ Å). It can be accounted for by the presence of direct interactions between filled t_{2g} orbitals bringing indeed an antiferromagnetic contribution which is absent for Ni^{2+} (i.e., d^8) ions. $Cs_3Fe_2F_9$ is thus an exceptional example for an iron(III) compound where predominant ferromagnetic interactions occur between some Fe^{3+} ions, an unexpected feature for a d^5 electronic configuration.

Acknowledgments

References

1. J. DARRIET, J. M. DANCE, AND A. TRESSAUD, J. Solid State Chem. 54, 29 (1984).

TABLE IV

COMPARISON OF THE BEST LEAST-SQUARE FITTED PARAMETERS FOR THE SUSCEPTIBILITY AT $T = 1.7$ K

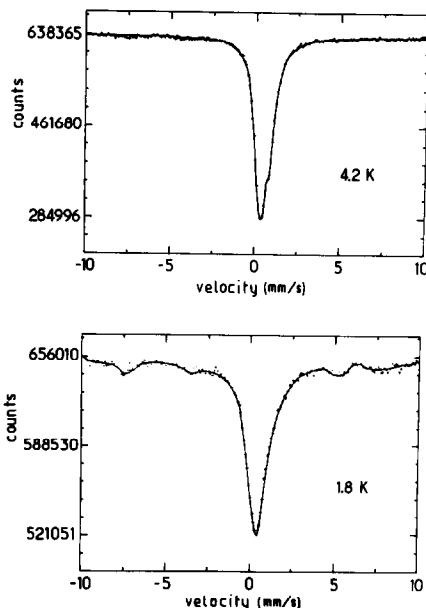|	$J/k = 0.98_3$ K $z'J''/k = 0.04_8$ K	$J/k = 0.98_3$ K $z'J''/k = 0$ K	$J/k = 0.35_1$ K $z'J''/k = 0$ K
$\chi_{exp} = 5.562$	5.685	8.904	8.563

2. J. M. DANCE, N. KERKOURI, J. DARRIET, AND A. TRESSAUD, *Mater. Lett.* **1,** 49 (1982).

3. J. DARRIET, E. BONJOUR, D. BELTRAN-PORTER, AND M. DRILLON, *J. Magn. Magn. Mater.* **44,** 287 (1984).

4. K. WALTERSSON, *Cryst. Struct. Commun.* **7,** 507 (1978).

5. F. WALL, G. PAUSEWANG, AND D. BABEL, *J. Less-Common Met.* **25,** 257 (1971).

6. R. MATTES, K. MENNEMANN, N. JÄCKEL, H. RIESKAMP, AND H. J. BROCKMEYER, *J. Less-Common Met.* **76,** 199 (1980).

7. R. MATTES AND H. FÖRSTER, *J. Less-Common Met.* **87,** 237 (1982).

8. M. RENNINGER, *Z. Phys.* **106,** 141 (1937).

9. D. T. CROMER AND J. D. MANN, *Acta Crystallogr. Sect. A* **24,** 321 (1968).

10. D. T. CROMER AND D. LIBERMANN, *J. Chem. Phys.* **53,** 1981 (1970).

11. R. E. SCHMIDT, M. BIRKAAHN, AND W. WASSA, STRUX, Programmsystem zur Verarbeitung von Röntgendaten, Marburg (1980).

12. G. M. SHELDRICK, SHELX 76, Program for Crystal Structure Determination, Cambridge (1976).

13. C. K. JOHNSON, ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL-3794, Oak Ridge, Tennessee (1965).

14. A. P. GINSBERG, R. L. MARTIN, R. W. BROOKES, AND R. C. SHERWOOD, *Inorg. Chem.* **11,** 2884 (1972).

15. J. DARRIET, J. L. SOUBEYROUX, H. TOUHARA, A. TRESSAUD, AND P. HAGENMULLER, *Mater. Res. Bull.* **17,** 315 (1982).

16. A. P. GINSBERG AND M. E. LINES, *Inorg. Chem.* **11,** 2289 (1972).

17. J. R. REGNARD, Private communication (1985).

18. S. J. PICKART AND H. A. ALPERIN, *J. Appl. Phys.* **39,** 1332 (1968); **42,** 1617 (1971).