

Ordered Magnetic Frustration: XVI. Magnetic Structure of CsCoF_4 at 1.5 K

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Received November 13, 1990

The crystal and magnetic structures of CsCoF_4 have been determined by means of neutron powder diffraction. The crystal structure is isostructural with $\beta\text{-RbAlF}_4$ and can be described as the stacking of unconnected tetragonal tungsten bronze type layers with Cs^+ cations in between. The strong anisotropy of $3d^6 \text{Co}^{3+}$ spins is responsible for a collinear magnetic structure, despite the presence of magnetic frustration. The competition between antiferromagnetic superexchange interactions within the triangular cycles of the structure is solved by the break of the weakest interaction, resulting in a parallel arrangement of spins connected by the AF interaction. This situation is compared with the one previously observed in KMnFeF_6 which exhibits a similar frustrating topology, but with isotropic interactions. © 1991 Academic Press, Inc.

1. Introduction

In the previous papers of this series, a number of ordered frustrated magnetic structures of fluorides have been presented (see Ref. (1) and references therein). Among them, the magnetic structure of the tetragonal tungsten bronze (TTB) like KMnFeF_6

(2) provides a good illustration of nontrivial spin arrangement resulting from magnetic frustration. CsCoF_4 , which has recently been isolated by two of us (3), has been shown to be isostructural with $\beta\text{-RbAlF}_4$ (4). This structure exhibits the same kind of TTB-type layers as KMnFeF_6 . It gives the opportunity to test the influence of spin anisotropy on a frustrating topology ($3d^6 \text{Co}^{3+}$ ($S = 2$) spins are highly anisotropic compared to $3d^5 \text{Mn}^{2+}$ or Fe^{3+} ($S = 5/2$) spins).

In this paper, the magnetic structure of CsCoF_4 as determined from neutron powder

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diffraction data is discussed in terms of magnetic frustration. For this purpose, the recently determined magnetic structure of another cobalt(III) fluoride, the unfrustrated dirutile LiCoF_4 (5), will give some precious hints on the magnetic behavior of high spin Co^{3+} cations.

The present paper is structured as follows: Section 2 is devoted to the experimental part of the work. The crystal and magnetic structures of CsCoF_4 are presented in Sections 3 and 4, respectively. Finally in Section 5, the magnetic structure of CsCoF_4 will be analyzed in terms of magnetic frustration.

2. Experimental

The powdered sample used for neutron diffraction experiments has been synthesized according to the procedure presented in (3).

Two neutron diffraction patterns were collected at 1.5 and 218 K on the powder diffractometer D1A of the High Flux Reactor of the Institut Laue Langevin at Grenoble. The wavelength was fixed at 1.909 Å and the full angular range ($0^\circ < 2\theta < 160^\circ$) was scanned in steps of 0.05° . The sample was contained in a cylindrical vanadium can ($\phi = 15$ mm) and the container was placed in a liquid helium cryostat with temperature regulation.

The structural refinements were performed by fitting the whole observed profile to a calculated profile of Gaussian peaks, according to the method introduced by Rietveld (6) and modified by Hewat (7). The nuclear scattering lengths and magnetic form factors were taken from Koester and Rauch (8) and Watson and Freeman (9), respectively.

3. Crystal Structure at 218 K

The crystal structure of CsCoF_4 at 218 K has been refined in the same space group

as $\beta\text{-RbAlF}_4$ ($I\bar{4}c2$), from the atomic positions of the latter (4). The true space group of $\beta\text{-RbAlF}_4$ has been discussed in (4), where two other possible space groups ($I4/mcm$ and $I4cm$) were eliminated on consideration of Hamilton ratios. These two other possibilities should not be excluded for CsCoF_4 . The poor quality of the diffraction data prevented us from distinguishing between these three space groups from diffraction data only. Therefore, due to the lack of any other information, we decided to refine the structure in the same space group as $\beta\text{-RbAlF}_4$.

During the refinement, the thermal factors of Co^{3+} cations were held fixed to 0.1 \AA^2 . The refined atomic positions are given in Table I and distances and angles in Table II. Observed and calculated profiles are presented in Fig. 1. The quality of fit is relatively poor ($R_I = 0.114$, $R_p = 0.195$, $R_{wp} = 0.195$, $R_{exp} = 0.133$). Two reasons can be put forward to justify it. First the poor quality of statistics of the pattern, because of the small amount of compound available due to the difficulty of synthesis. Second, the presence of a small amount of impurity (marked by a star on Fig. 1). For these reasons and given the uncertainty on the true space group, the very small Co2-F3 calculated distance (see Table II) should not be considered dramatic. Moreover, the mean Co-F distances, about 1.92 Å, are in very good agreement with the distances determined in LiCoF_4 (5) and with ionic radii of Co^{3+} (high spin) and F^- as given by Shannon and Prewitt (10).

The refined structure is shown in Fig. 2. It can be described as the stacking of unconnected shifted layers of the TTB type, isolated by Cs^+ cations. As already shown in KMnFeF_6 (2), this type of topology implies magnetic frustration when coupling interactions are antiferromagnetic, which is often the case with 180° -type superexchange paths between transition metal cations. This point will be confirmed by the study of the magnetic structure of CsCoF_4 .

TABLE I
CELL PARAMETERS AND ATOMIC POSITIONS OF CsCoF₄ at 218 K and 1.5 K (in Brackets)

Atom	(site)	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Cs1	(4a)	0	0	$\frac{1}{4}$	0.29(23) [0.47(18)]
Cs2	(16i)	0.3499(7) [0.3433(9)]	0.8282(7) [0.8341(9)]	0.6816(5) [0.6799(3)]	1.32(17) [1.36(13)]
Co1	(4d)	$\frac{1}{2}$	0	0	0.1 [0.102(1)]
Co2	(16i)	0.7918(12) [0.7932(8)]	0.0725(11) [0.0749(8)]	0.9833(10) [0.9861(9)]	0.1 [0.099(1)]
F1	(16i)	0.3421(7) [0.3432(5)]	0.9999(5) [0.0014(3)]	0.9947(9) [0.9899(7)]	1.59(13) [0.69(10)]
F2	(16i)	0.1397(5) [0.1412(4)]	0.0661(6) [0.0655(4)]	0.9843(7) [0.9912(8)]	1.17(17) [0.78(11)]
F3	(16i)	0.0755(11) [0.0767(10)]	0.2072(12) [0.2094(13)]	0.1409(7) [0.1444(6)]	2.32(25) [0.90(18)]
F4	(16i)	0.9193(11) 0.9197(10)	0.7909(12) 0.7912(13)	0.8616(7) 0.8632(6)	2.38(29) [1.45(22)]
F5	(8h)	0.2196(5) [0.2208(4)]	0.7196(5) [0.7208(4)]	$\frac{1}{2}$	0.19(19) [1.03(16)]
F6	(8g)	0	$\frac{1}{2}$	0.1419(8) [0.1433(6)]	2.56(22) [1.40(15)]

Note. Space group $\bar{I}4c2$, $Z = 20$, $a = b = 12.4476(6)$ Å [12.4353(4)], $c = 12.9277(7)$ Å [12.8612(5)], $V = 2003.05(30)$ Å³ [1988.81(19)].

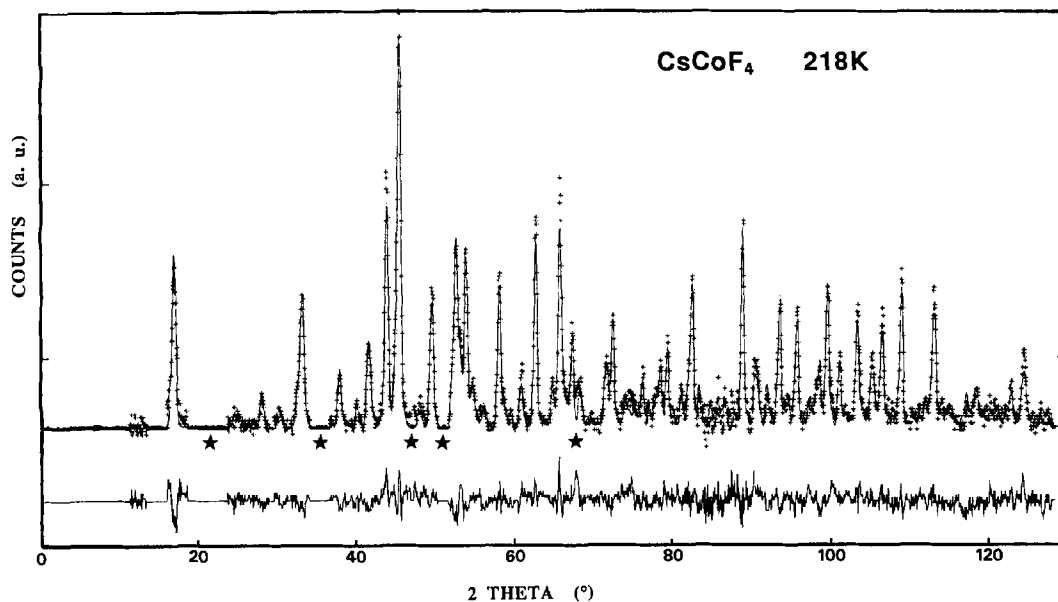


FIG. 1. Observed (+) and calculated (line) neutron diffraction profiles for CsCoF₄ at 218 K. The difference profile (obs - calc) at the same scale is shown at the bottom of the figure. The stars show the positions of impurity peaks (most of them have been excluded for the final refinement). Peak indexation is given in Fig. 4.

TABLE II
 INTERATOMIC DISTANCES (Å) AND CHARACTERISTIC ANGLES (°) IN CsCoF₄ AT 218 K AND 1.5 K (IN BRACKETS)

Octahedron [CoF ₆]					
Co1-F1	4 × 1.967(9)	[1.954(6)]	F1-Co1-F1	176.0(5)	[172.4(4)]
Co1-F6	2 × 1.834(10)	[1.843(8)]	F6-Co1-F6	180	[180]
⟨Co1-F⟩	1.920	[1.917]	F1-Co1-F1	90.0(3)	[91.3(2)]
			F1-Co1-F1	90.1(3)	[89.2(2)]
			F1-Co1-F6	88.0(3)	[86.2(3)]
			F1-Co1-F6	92.0(3)	[93.8(3)]
Octahedron [Co2F ₆]					
Co2-F1	1.900(17)	[1.944(11)]	F1-Co2-F2	163.2(9)	[169.2(8)]
Co2-F2	1.925(16)	[1.928(11)]	F2-Co2-F5	173.6(8)	[172.9(7)]
Co2-F2	2.001(16)	[1.963(11)]	F3-Co2-F4	175.8(11)	[176.7(9)]
Co2-F3	1.606(16)	[1.679(14)]	F1-Co2-F2	87.9(6)	[85.8(4)]
Co2-F4	2.008(16)	[1.940(14)]	F1-Co2-F3	95.5(9)	[90.9(7)]
Co2-F5	2.051(15)	[2.033(11)]	F1-Co2-F4	86.7(8)	[88.9(7)]
⟨Co2-F⟩	1.915	[1.915]	F1-Co2-F5	91.8(7)	[92.7(5)]
			F2-Co2-F2	89.0(7)	[89.8(5)]
			F2-Co2-F3	91.4(9)	[93.1(8)]
			F2-Co2-F3	101.1(9)	[99.2(7)]
			F2-Co2-F4	77.0(7)	[81.3(6)]
			F2-Co2-F4	92.4(8)	[90.2(7)]
			F2-Co2-F5	89.6(6)	[90.5(5)]
			F3-Co2-F5	95.0(8)	[93.9(7)]
			F4-Co2-F5	81.2(6)	[82.9(6)]
Polyhedra [CsF ₁₂] (<i>d</i> < 3.7 Å)					
Cs1			Cs2		
Cs1-F2	4 × 3.588(9)	[3.657(9)]	Cs2-F1	3.229(12)	[3,187(11)]
Cs1-F3	4 × 3.086(14)	[3.088(15)]	Cs2-F1	2.953(13)	[2.917(11)]
Cs1-F4	4 × 3.141(14)	[3.140(14)]	Cs2-F2	3.346(11)	[3.447(12)]
⟨Cs1-F⟩	3.272	[3.295]	Cs2-F3	3.140(14)	[3.018(13)]
			Cs2-F3	3.484(16)	[3.390(17)]
			Cs2-F3	3.230(16)	[3.322(17)]
			Cs2-F4	3.642(17)	[3.532(19)]
			Cs2-F4	3.216(17)	[3.269(19)]
			Cs2-F4	2.891(14)	[2.981(13)]
			Cs2-F5	3.158(9)	[3.108(9)]
			Cs2-F6	3.643(10)	[3.636(10)]
			Cs2-F6	2.886(9)	[2.877(11)]
			(Cs2-F)	3.235	[3.224]
Co-Co distances (nearest neighbors) and Co-F-Co superexchange angles					
Co1-Co2	3.749(15)	[3.767(10)]	Co1-F1-Co2A	151.6(6)	[150.2(4)]
Co2A-Co2B	3.885(20)	[3.856(14)]	Co2A-F2-Co2A	168.3(8)	[173.4(8)]
Co2B-Co2B	3.905(20)	[3.885(14)]	Co2A-F5-Co2B	142.5(6)	[142.9(4)]

4. Magnetic Structure at 1.5 K

From magnetic susceptibility measurements (11), CsCoF₄ exhibits an antiferromagnetic behavior below $T_N = 54$ K. This

is consistent with a high spin $3d^6$ electronic configuration of Co³⁺ cations, as suggested by the mean Co-F distances (see previous section).

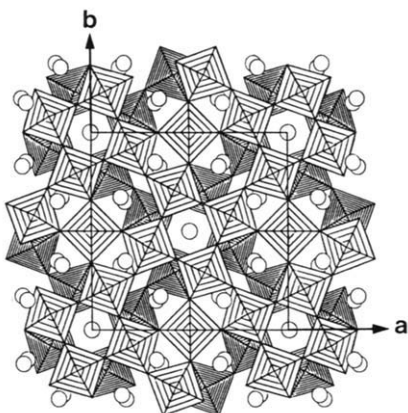


FIG. 2. The crystal structure of CsCoF₄. Two successive unconnected TTB layers along the *c* axis are represented by different hatching of [CoF₆] octahedra. Cs⁺ cations are drawn as circles.

Compared to the high temperature diffraction pattern, the low temperature (1.5 K) pattern exhibits new peaks and the enhancement of some already existing ones. The new peaks can be indexed in the nuclear cell and satisfy the I lattice condition. We tried to determine the most probable coupling modes in CsCoF₄ from the previous considerations and also from what is already known concerning other Co³⁺ fluorides like LiCoF₄ (5). In this last compound, the anti-ferromagnetic arrangement of spins in the perovskite layers confirms the AF nature of the 180° type Co³⁺-F⁻-Co³⁺ superexchange interaction. This should lead, first to the presence of magnetic frustration in the triangular platelets of CsCoF₄, and second to a strict AF arrangement of spins in the square platelets of the structure. Besides, in LiCoF₄, the magnetic moments of Co³⁺ cations are aligned perpendicular to the perovskite layers of the structure. We will assume that the direction perpendicular to the layers (TTB layers in CsCoF₄) is also a direction of easy magnetization in CsCoF₄. Therefore, the main assumption of our model is that the strong anisotropy of 3d⁶ cations overcomes a possible noncollinearity due to magnetic frustration.

Thus, our model will satisfy the following conditions:

(i) The spins are aligned along the *c* direction of the tetragonal cell.

(ii) The arrangement of spins is strictly AF in the square platelets of the structure.

(iii) Due to the presence of magnetic frustration, the three sites at the corners of triangular platelets are considered independent. This means that the Co2 site is split into two independent sites called Co2A and Co2B (Fig. 3 shows the three Co³⁺ sublattices in a TTB layer).

(iv) The lattice condition I is active (two spins deduced by a translation $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ are arranged ferromagnetic).

These conditions allow the definition of the coupling modes within each sublattice. They are given in Table III. They correspond (12) to the magnetic space group *I4'*.

This model, assuming magnetic moments along the *c* axis of the structure, has been

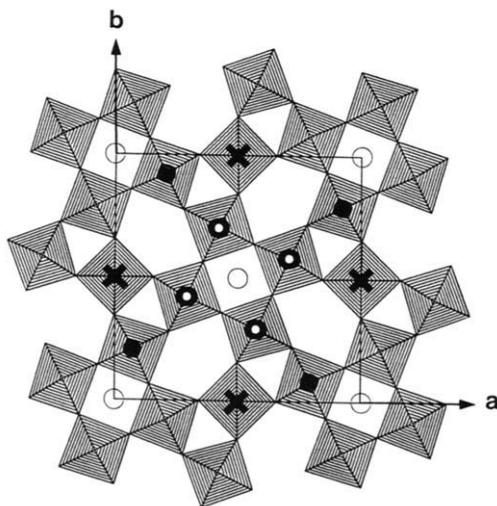


FIG. 3. The three independent cobalt sites (Co1, Co2A, and Co2B) taken into account in the model used to determine the magnetic structure of CsCoF₄ (x = Co1, ● = Co2A, ○ = Co2B).

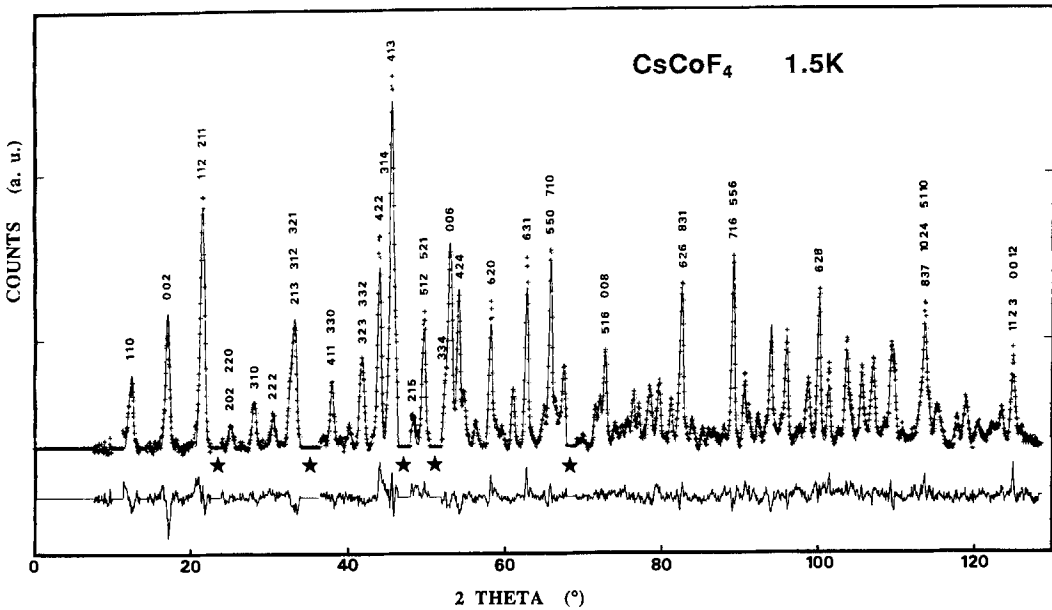


FIG. 4. Same as Fig. 1, with the diffraction pattern recorded at 1.5 K.

tested by comparison with the low temperature diffraction pattern (Fig. 4). The refinement quickly converged toward the values of magnetic moments given in Table IV, with the reliabilities

$$R_I = 0.095 (R_{\text{nuc}} = 0.094, R_{\text{mag}} = 0.105),$$

$$R_p = 0.142, R_{wp} = 0.147 (R_{\text{exp}} = 0.092).$$

The saturated magnetic moments are slightly smaller than the expected value for a d^6 cation ($4 \mu\text{B}$) and than the observed value in unfrustrated LiCoF_4 ($3.62 \mu\text{B}$). Such a reduction of saturated magnetic moments has already been observed in many frustrated magnetic structures (see for instance (13)).

The same kind of model of coupling

TABLE III
COUPLING MODES IN THE MODEL USED FOR THE DETERMINATION OF THE MAGNETIC STRUCTURE OF CsCoF_4

Co1		Co2 (A and B)			
Atomic positions	Coupling	Atomic positions			Coupling
$0 \frac{1}{2} 0$	+	x	y	z	+
$\frac{1}{2} 0 0$	-	$-x$	$-y$	z	+
$\frac{1}{2} 0 \frac{1}{2}$	+	y	$-x$	$-z$	-
$0 \frac{1}{2} \frac{1}{2}$	-	$-y$	x	$-z$	-
		$\frac{1}{2} + x$	$\frac{1}{2} + y$	$\frac{1}{2} + z$	+
		$\frac{1}{2} - x$	$\frac{1}{2} - y$	$\frac{1}{2} + z$	+
		$\frac{1}{2} + y$	$\frac{1}{2} - x$	$\frac{1}{2} - z$	-
		$\frac{1}{2} - y$	$\frac{1}{2} + x$	$\frac{1}{2} - z$	-

TABLE IV
REFINED MAGNETIC MOMENTS (μB) IN CsCoF_4 AT 1.5 K

Atoms	Atomic positions			Magnetic moments		
	x	y	z	M_x	M_y	M_z
Co1	$\frac{1}{2}$	0	0	0	0	3.50(12)
Co2A	0.7932	0.0749	0.9861	0	0	-2.84(58)
Co2B	0.7932	0.9251	0.4861	0	0	3.46(59)

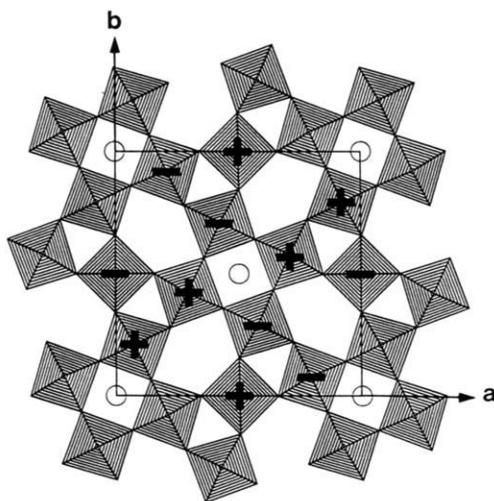


FIG. 5. The magnetic structure of CsCoF₄ at 1.5 K (only one TTB layer has been drawn). Magnetic moments are aligned along the *c* axis of the structure. The moments carried by Co³⁺ cations located in an adjacent TTB layer are deduced according to the coupling modes presented in Table III.

modes, but with moments lying in the (*a*,*b*) plane, has also been tested. It gives a much worse reliability and unlikely moment values. These results confirm the correctness of the model presented above. The magnetic structure of CsCoF₄ is shown on Fig. 5. In adjacent TTB layers, spins deduced by a translation $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ are aligned ferromagnetically.

5. Discussion

The antiferromagnetic nature of all interactions between nearest magnetic neighbors in CsCoF₄ can easily be deduced from a comparison with LiCoF₄. It is well known that, in such compounds, the magnetic coupling is governed by superexchange interactions through fluorines. The linear dependence of the interaction strength on $\cos^2 \theta$, where θ is the superexchange angle, has already been pointed out several times

(14–17). The strength of the AF interaction is maximum when θ equals 180° and decreases when θ decreases. Eventually, the interaction can even become ferromagnetic when θ approaches 90° (18). The superexchange angle Co³⁺–F[–]–Co³⁺ in the unfrustrated layers of LiCoF₄ is 134° (5). From the AF magnetic structure of this compound, the AF character of the Co³⁺–F[–]–Co³⁺ superexchange interaction is obvious. Comparatively, all the superexchange angles in CsCoF₄ are greater than 140° (see Table II). Following the $\cos^2 \theta$ law, it means that all superexchange interactions in CsCoF₄ are antiferromagnetic and stronger than in LiCoF₄. It confirms the presence of magnetic frustration in the triangular cycles of the structure.

This situation can be compared to the one in KMnFeF₆, where the same kind of frustrated magnetic behavior has already been evidenced (2). The difference between these compounds lies in the isotropic character of Mn²⁺ and Fe³⁺ spins compared to the strong anisotropy of Co³⁺ spins, as stressed by the collinear magnetic structure of CsCoF₄. The former case has thus already been modeled with an *XY* spin model (2) while the latter is more consistent with an Ising model.

Therefore, the frustration problem in CsCoF₄ reduces to the behavior of a triangular platelet of Ising spins with AF interactions. This problem is trivial and its solution depends on the relative strength of the interactions. The enumeration given by Liebmann in his review about frustrated Ising systems (19) can be recalled here. Three cases are to be distinguished, depending on the relative strength of interactions J_1 , J_2 , and J_3 (see Fig. 6).

(i) $J_1 \leq J_2 < J_3 < 0$, the weakest interaction (J_3) is broken at $T=0$. The degeneracy is 2, as for the ferromagnetic case. The spin configuration is given in Fig. 6a.

(ii) $J_1 < J_2 = J_3 < 0$, one of the two interactions J_2 or J_3 is broken at $T=0$. The degeneracy

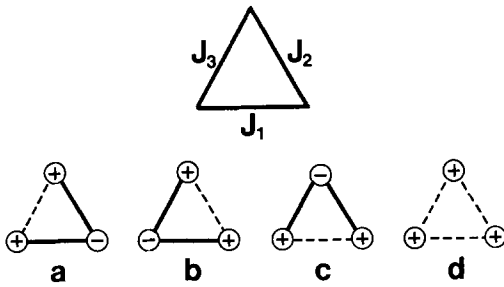


FIG. 6. The four possible spin configurations of a triangular platelet of Ising spins. Broken lines symbolize broken interactions, assuming all three interactions are antiferromagnetic.

acy is 4 and the ground state configurations are given in Figs. 6a and 6b.

(iii) $J_1 = J_2 = J_3 < 0$, one of the three interactions is broken at $T = 0$. The degeneracy is 6, with ground state configurations *a*, *b*, and *c* of Fig. 6.

The ground state of the triangular platelet with Ising spins and equal AF interactions is fully degenerate (iii). Six among the eight possible spin configurations correspond to the ground state energy (*a*, *b*, *c*, and their opposite configurations). For this reason, no long range ordering transition is possible in the triangular lattice with equal AF interactions and Ising spins. On the contrary, when two of the interactions are equal, a long range order is observed in the lattice: a 1D-type ordering at $T = 0$ if the third interaction is the strongest (ii); a 2D-type ordering at $T > 0$ if the third interaction is the weakest (i).

In real compounds, the realization of case (iii), with three equal interactions usually demands a rhombohedral or hexagonal crystal symmetry (the equivalence of the three interactions derives from the presence of a three-fold symmetry axis). For crystals with lower symmetry, the absence of a three-fold axis lifts the degeneracy (i and ii). This happens in CsCoF_4 which has a tetragonal symmetry. In every triangular platelet of the

lattice (Fig. 7) two magnetic interactions originate from identical superexchange angles: $\theta(\text{Co1-F-Co2A}) = \theta(\text{Co1-F-Co2B}) = 150^\circ$, the third angle being $\theta(\text{Co2A-F-Co2B}) = 143^\circ$. By considering the $\cos^2 \theta$ law of coupling constants, the last interaction should be weaker than the two former, which are equal. Case (i) is thus realized, where degeneracy is minimum and the platelet ordered, as confirmed by the observed ordered magnetic structure at low temperature. As already mentioned, the unsatisfied (broken) interaction should be the weakest one, namely the interaction between Co2A and Co2B, resulting in a parallel alignment of spins. This is exactly what is observed in the magnetic structure of CsCoF_4 , which is therefore fully consistent with our assumptions and with the refined crystal structure.

We checked the main points of our reasoning by simulating with the program MCMAG (20) the magnetic structure of TTB-like layers of Ising spins in AF interaction. The results are in very good agreement with our conclusions and with the refined magnetic structure of the compound. The only degeneracy observed during several runs of the simulation concerns the global direction of spins (degeneracy = 2). This is

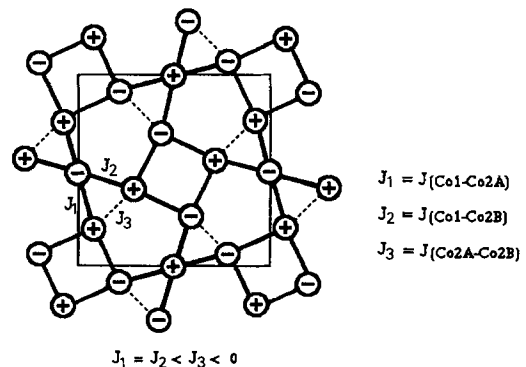


FIG. 7. The frustrating topology of CsCoF_4 . Broken lines correspond to broken interactions (AF $J_{(\text{Co2A-F-Co2B})}$ connecting parallel spins).

the discrete equivalent to the rotation degeneracy of an XY model (2).

6. Conclusion

The frustrated magnetic structure of CsCoF₄ emphasizes the strong magnetic anisotropy of Co³⁺ cations, which is responsible for a broken AF interaction. The results presented above show that, due to magnetic frustration, the same topology of magnetic interactions can lead to totally different magnetic structures depending on the anisotropy of the spin system. Beside theoretical evidence, such conclusions can be drawn from the comparison with other compounds such as KMnFeF₆ (2) and should be confirmed by the determination of the magnetic structures of other frustrated fluorides, particularly of β-CsFeF₄ (3), which is isostructural to CsCoF₄.

Acknowledgments

Two of us (T.F. and R.H.) sincerely thank the Deutsche Forschungsgemeinschaft, Bonn, and the Fonds der Chemischen Industrie, Frankfurt am Main, for the support of this work.

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