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Jahn-Teller ordering in Kagomé-type layers of compounds $A_2A'Mn_{3}^{111}F_{12}$ (A = Rb, Cs; A' = Li, Na, K)¹

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Abstract

For a series of new Mn(III) fluorides the crystal structures have been determined by X-ray diffraction on single crystals: $Cs_{1}LiM_{1}F_{12}$, space group $R\bar{3}$, Z = 3 (merchedral twin), a = 7.440(1), c = 17.267(3) Å, R = 1.95%; three isostructural triclinic phases, space group $P\bar{1}$, Z = 2, $Cs_{2}NaMn_{3}F_{12}$, a = 7.05(1), b = 7.512(1), c = 10.376(2) Å, $a = 89.89(3)^{\circ}$, $\beta = 87.32(3)^{\circ}$, $\gamma = 89.89(3)^{\circ}$, R = 2.75%; $Rb_{2}NaMn_{3}F_{12}$, a = 7.115(1), b = 7.482(1), c = 10.160(2) Å, $a = 89.92(3)^{\circ}$, $\beta = 87.52(3)^{\circ}$, $\gamma = 89.51(3)^{\circ}$, R = 2.70%; $Rb_{2}NaMn_{3}F_{12}$, a = 6.883(1), b = 7.481(1), c = 10.194(2) Å, $a = 89.92(3)^{\circ}$, $\beta = 87.16(3)^{\circ}$, $\gamma = 90.25(3)^{\circ}$, R = 4.87%; monoclinic $Cs_{2}KMn_{3}F_{12}$, space group C2/c, Z = 4, a = 13.112(3), b = 7.571(2), c = i2.672(3) Å, $\beta = 108.79(3)^{\circ}$, $R = 5.3^{\circ}$. All structures derive from the $Cs_{2}NaA1_{3}F_{12}$ parent structure and consist of $[Mn_{3}F_{12}]$ layers of corner-sharing octahedra of the Kagomé-net-type (3+6 octahedra units like in the hexagonal tungsten bronze layers). The [MnF_{6}] octahedra are strongly elongated by the Jahn-Teller effect with ratios of long to short axes of about 1.15. In all structures the long axes are oriented within the layers in an alternating wind-wheel-like pattern corresponding to an antiferrodistorive Jahn-Teller ordering. Thus, all Mn-F-Mn bridges are asymmetric; the bridge angles are between 136° and 141°. Magnetic investigations of $Cs_{2}NaMn_{3}F_{12}$ and $Cs_{2}KMn_{3}F_{12}$ indicate similar antiferromagnetic exchange interactions (J/k = -2.5 K), but only for the $Cs_{2}K$ compound has 2D and 3D ordering been found at low temperatures. The results are discussed in context with the Jahn-Teller ordering and the 'trustrated' exchange situation in the Kagomé net.

Keywords: Manganese(III); Jahn-Teller ordering: Fluoromanganates(III); Crystal structures; Magnetism

1. Introduction

Octahedral complexes of transition metal ions in a d⁴ (high spin), d⁷ (low spin) or d⁹ configuration usually show anomalous structural properties because of the unequal occupation of e_s orbitals $(e_s^1 \text{ or } e_s^1)$ giving rise to anisotropic σ -antibonding properties. In a crystal, the vibronic coupling between the electronic system and the lattice modes results in an ordering pattern of valence electrons (here e_s electrons) connected with a regular distortion pattern of the structure ('Jahn-Teller ordering'). This is the special case of a strong ground term [1-3].

In the past few years we have investigated a series of fluorine compounds of Mn(III) (d⁴ high spin) which proved to be very suitable model systems for studies of the interdependence of structural type and Jahn-Teller ordering. In addition, their pronounced tendency to build 1D or 2D structures allows for investigations of the magnetic exchange properties that are strongly influenced by the electronic ordering. One main topic concerned compounds with linear chain $[MnF_s]^2^$ anions (e.g. Refs. [4,5]), a second one AMnF₄ compounds (A = alkali metal) with quadratic $[MnF_4]^$ layers (e.g. Refs. [6,7]). Here we report on a new class of Jahn-Teller distorted structures with $[MnF_4]^$ layers deriving from the Kagomé-net-type in the compounds A₂A/Mn₃F₁₂ (A₂A' = alkali metal).

2. Experimental

Brown-red powder samples and small crystals of compounds $A_2A'Mn_3F_{12}$ with combinations $A_2A' =$ Cs_2Li , Cs_2Na , Cs_2K and Rb_2Li , Rb_2Na could be prepared by heating mixtures of the binary fluorides at $820^{\circ}C$ or $720^{\circ}C$ (Cs_2K , Rb_2Na) in sealed platinum tubes. MnF, was claimed from NH₄MnF₃ by fluorination with F₂ at 470 °C. CsF and RbF were prepared by

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Dedicated to Professor Dr. Kurt Dehnicke on the occasion of his 65th birthday.

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thermal decomposition of the bifluorides $CsHF_2$ (at 500 °C) and $RbHF_2$ (at 600 °C) formed from the carbonates (Merck, p.a.) which were dissolved in 40% HF. For the other alkali fluorides commercial products (Merck, p.a.) were used. The purity of the samples was examined by analyses of the fluorine contents and by X-ray powder diffractometry.

The single crystal X-ray investigations were performed on Buerger precession cameras (Enraf-Nonius, Mo Ka radiation) and a four-circle diffractometer (CAD4, Enraf-Nonius, Mo Ka radiation, graphite monochromator). The lattice constants were determined from the diffraction angles of 25 highangle reflections measured in the positive and negative 2θ range. For data collections ω -sce , were used. An LP correction and an empirical absorption correction based on Ψ -scans were applied. The structures have been solved by Patterson techniques or refined starting from analogous structure models. Scattering factors for neutral atoms and contributions of anomalous dispersion have been taken from Ref. [8]. The calculations have been done in the SHELXTL-PLUS system [9]. the structures were refined by full matrix least squares methods using the F^2 data [10]. More details are given in the tables of the following section.

3. Crystal structures

A compound $A_2A'M_3^{11}F_{12}$ was first described and its structure determined by Courbion et al. (Cs₂NaAl₃F₁₂ [11,12]). The structure is rhombohedral,

Table 1

Experimental data for the crystal structure	e determinations of A ₂ A'Mn ₃ F ₁₂	compounds
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space group $R\bar{3}m$ and may be interpreted as an order variant of the pyrochlore-related RbNiCrF₆ type [13]. Ordered substitution of 1/4 of the octahedral sites by a smaller alkali metal ion (here Na) changes the 3D pyrochlore network to a Kagomé-type layer structure (for a further discussion of structural relationships of the weberites and fluorite see Ref. [14]). Later, other compounds $A_2A'M_3^{MT}F_{12}$ were prepared with $M^{TH} =$ Ti, V, Cr, Fe, Co, Sc, Ga and other combinations of alkali metals [15–17]. However, recently, another two single crystal structure determinations were reported showing monoclinic variants for K₂NaAl₃F₁₂ and Rb₂NaAl₃F₁₂ [17].

For all our Mn(III) compounds crystals could be grown but, similar to the latter Al compounds, the structure determinations were rather difficult due to twinning or pseudo-symmetry problems. Three different structure variants were encountered which are discussed below. The experimental data are collected in Table 1.

3.1. Structure of twinned Cs₂LiMn₃F₁₂

For the Cs₂Li compound a rhombohedral unit cell was found (Table I) similar to that of Cs₂NaAl₃F₁₂ [12]. The Laue group seemed to be 3m ($R_{int} = 0.044$) and an analogous structure model in the space group R3m could be refined successfully. A very small resulting temperature factor for the Li atom suggested a possible partial disorder with Mn on the octahedral positions. Indeed, a split atom model containing 6.5% Mn at the Li site, and vice versa, led to rather good results with a residual of $wR_2 = 7.3\%$ (for all reflec-

Formula	Cs ₂ LiMn ₃ F ₁₂	Cs ₂ NaMn ₃ F ₁₂	Rb ₂ NaMn ₃ F ₁₂	Rh ₂ LiMn ₃ F ₁₂	Cs ₂ KMn ₃ F ₁₂
Formula weight	665.58	681.63	586,75	570.70	697.74
Crystal size (mm')	$0.12 \times 0.07 \times 0.02$	$0.15 \times 0.12 \times 0.05$	0.30×0.25×0.09	0.10×0.07×0.02	0.15×0.10×0.05
Absorption coeff. μ (cm ⁻¹)	100.2	97.6	125.9	129.3	96.4
Ψ-scan corr., T	0.99, 0.57	0.77, 0.66	0.96. 0.57	0.99, 0.66	0.88. 0.54
Space group	R3, Z = 3	$P\bar{1}, Z = 2$	PĪ, Z = 2	$P\bar{1}, Z = 2$	C2ic, Z = 4
Lattice constants (Mo Ka)					
a (À)	7.440(1)	7.305(1)	7.115(1)	6.883(1)	13.112(3)
ь(A)		7.512(1)	7.482(1)	7.481(1)	7.571(2)
c (Å)	17.267(3)	10.376(2)	10.160(2)	10.194(2)	12.672(3)
ar (deg)		89.89(3)	89.92(3)	89.42(3)	
A (deg)		87.32(3)	86.52(3)	87.16(3)	108.79(3)
y (deg)		89.89(3)	89.51(3)	90.25(3)	
Density d. (g cm ⁻¹)	4.006	3.980	3.610	3.615	3,892
Measuring range θ (deg)	3-28, h.±k,±l	$2-28, h, \pm k, \pm 1$	$2-27, \pm h, -k, \pm l$	$2-27, \pm h, -k, \pm l$	3-25, ±h,k,±l
Reflections					,
total,	2853	2173	2360	2307	2053
unique, $>2\sigma(I)$	446, 400	2002, 1557	2187, 1855	2139, 1132	1031, 859
Parameters	32	170	170	171	87
Residuals wR ₂ [*] , R [*]	0.0443, 0.0195	0.0502, 0.0275	0.0732, 0.0270	0.1068, 0.0487	0.1321, 0.0530
$\Delta \rho_{\text{Rax,min}}$ (c Å ⁻¹)	1.03, -0.39	0.81, -0.55	0.54 0.59	i.17, -0.998	3.711.51

* For all reflections: * for the observed reflections (> $2\sigma(I)$).

tions), corresponding to a conventional R = 2.3% for the observed reflections only $(F_o > 4\sigma(F))$.

The resulting structural feature has two anomalies: the anisotropic displacement ellipsoid of the bridging F2 atom is somewhat large in the bond direction, and the coordination geometry at the Jahn-Teller ion Mn(III) is that of a compressed octahedron $(2 \times Mn -$ F1 = 1.804(1) Å, $4 \times Mn - F2 = 1.992(1)$ Å). This is very unusual, as all hitherto known structures with $[MnF_6]^{3-}$ units show strongly elongated octahedra. Thus, it seemed probable that the mirror plane of space group $R\bar{3}m$ providing symmetric bridges Mn-F2-Mn and four equal equatorial distances is really absent. The real space group is then the maximal subgroup $R\bar{3}$ and the high Laue group $\bar{3}m$ may be pretended by merohedral reflection twinning with the missing mirror plane (120) as twin element. A corresponding twin model of a structure with asymmetric bridges refined very well (program SHELXL-93 [10]) resulting in a twin ratio of 0.48(1), nearly 1:1, and still somewhat better residuals of $wR_2 = 4.41\%$ and R =1.95%. There is no doubt that this model gives the correct description of the structure, especially as analogous geometries have been found later on at un-twinned crystals of all other A2A'Mn3F12 compounds. The resulting atomic parameters are given in Table 2.

Fig. 1 shows that now, in contrast to the previous feature, the $[MnF_{4}]$ octahedra are elongated. Their geometry resembles that in the AMnF₄ layer structures [6]. The bond lengths and angles are given in Table 3. The topology of the Kagomé net allows — like the quadratic net — an order of elongated octahedra so that always long axes alternate with short axes. This Jahn-Teller ordering pattern, resembling a wind-wheel when we look at a hexagonal mesh, corresponds to the antiferrodistortive ordering nesh, corresponds to the antiferrodistortive ordering to the in the AMnF₄ compounds (Fig. 2). It is this ordering type that is found in Cs₂LiMn₃F₁₂ (Fig. 1).

Recently, a similar structure with a Jahn-Teller ion has been found in $Cs_2Cu_3M^{1V}F_{12}$ ($M^{1V} = Zr$, Hf) [18]. It contains layers of the Kagomé-net-type formed by [$Cu^{11}F_6$] octahedra. In contrast to our structures, these layers are connected by the M^{1V} ions instead of by the

Table 2 Atomic fractional coordinates and equivalent isotropic temperature factors (λ^2) for Cs,LiMn,F₁₂

Atom	x	y	z	U.,
Cs	0.0	0.0	0.12859(2)	0.03321(15)
Mn*	0.5	0.0	0.0	0.0113(2)
FL	0.4561(11)	0.5261(11)	0.10126(11)	0.0278(6)
F2	0.4103(4)	0.1850(7)	0.02408(15)	0.0246(7)
Li ^h	0.0	0.0	0.5	0.018(3)

 U_{va} is one-third of the trace of the orthogonalized U_{ij} tensor.

" Occupied by 2.17% Li, b occupied by 6.5% Mn.



Fig. 1. Section of the $[MnF_4]^-$ layer in Cs₂LiMn₃F₁₂ refined as a twin in space group $R\bar{3}$. The elongated octahedrał axes are drawn black. Thermal ellipsoids at the 50% probability level.

alkali metal ions. Thus, the structure is really 3D connected and the Jahn-Teller distortion is perpendicular to the Kagomé layer, because now the Cu-F- M^{IV} bridging provides the weakest Cu-F bond. In the $A_2A'Mn_3F_{12}$ compounds, the bridging bonds Mn-F-Mn within the Kagomé layers are the weakest. These examples again confirm the observation that in a certain structure type the Jahn-Teller distortion (normally an elongation) always occurs along the weakest bond axis. In the case of ambiguities, like in the quadratic AMnF₄ or Kagomé-type $A_2A'Mn_3F_{12}$ layer structures where two weak bond axes are present in the layers, an antiferrodistortive ordering is favoured providing asymmetric bridges.

The bridge angles Mn-F-Mn in $Cs_2LiMn_3F_{12}$ are 137.9(1)°, a typical value for a pyrochlore-like network. In fact, the Li atoms connecting the 2D [MnF₄] layers to form the ordered 3D pyrochlore network are in a nearly undistorted octahedral coordination (Li-F 2.039(2) Å, F-Li-F 87.7/92.3°) which is similar in size to the [MnF₆] octahedra. It is therefore not surprising that a partial mutual substitution (here 6.5%) of the

Table 3	
Salacted interstomic distances	(Å) and anoles (dea) in Cs LiMa

Selected intera	tomic distances (A	 and angles (deg) in CS ₂ Limin ₃ P ₁₂
Mn-F1	2×1.807(4)	Li-F	6×2.039(2)
Mn-F2	2×1.852(4)	Cs-F2	3×3.533(3)
Ma-F2'	2×2.133(4)	Cs-Fl	3×3.711(8)
		Cs-F1'	3×3.736(3)
		Cs-F1"	3×3.843(8)
F1-Mn-F2	88.3(2)	Mn-F2-Mn'	137.9(1)
F1'-Mn-F2	87.4(2)		
F1-Mn-F2'	91.7(2)	F1-Li-F1'	3×87.71(8)
F1'-Mn-F2'	92.6(2)	F1LiF1"	3×92.29(8)
F2-Mn-F2'	87.9(1)	F1'-Li-F1"	3×180
F2'-Mn-F2	92.0(1)		



Fig. 2. Scheme of antiferrodistortive ordering of elongated octahedra in the quadratic layer structures of $AMnF_4$ compounds (left) and the corresponding ordering in the $A_2A'Mn_3F_{12}$ compounds (right).

octahedral Li and Mn sites is observed. Attempts to prepare completely ordered samples for magnetic investigations failed. The Li-F distance agrees well with the sum of the Shannon [19] ionic radii (2.045 Å).

The coordination of the Cs atoms is 6+12, as in the pyrochlore parent structure. It may be described as a trigonally distorted octahedron where each of the 12 edges is capped by an additional fluorine atom (Fig. 3).

The Cs atoms are situated above and below the



Fig. 3. Coordination of caesium between two layers.

large six-membered octahedral meshes of the Kagomé net. The stacking of layers is ABCABC according to the rhombohedral space group. Thus, from the neighbouring layers the triangular groups are further coordinated to the Cs at ms.

In the AMnF₄ compounds the bridging angles Mn– F–Mn could be tuned by variation of the A counter cation leading to dramatic changes of magnetic properties from ferro- to antiferromagnetism [6.7]. We were thus interested to see whether a similar behaviour occurs at the Kagomé net layer structures. Therefore, the influence of variation of the A_2A' counter cations has been invest ated too.

3.2. Triclinic structures of $Cs_2NaMn_3F_{12}$, $Rb_2NaMn_3F_{12}$ and $Rb_2LiMn_3F_{12}$

Single crystal investigations on these three compounds claimed triclinic lattices with primary monoclinic and secondary rhombohedral pseudosymmetry. The crystal data are compiled in Table 1. The triclinic lattice constants are related to the rhombohedral cell (hexagonal setting) of $Cs_2LiMn_3F_{12}$ by

$$a_{1} \sim -2/3a_{h} - b_{h}/3 - c_{h}/3; b_{t} \sim b_{h};$$

$$c_{1} \sim -4/3a_{h} - 2/3b_{h} + c_{h}/3$$

They correspond to the monoclinic cells found for the Al compounds $Rb_2 naAl_3F_{12}$ and $K_2 NaAl_3F_{12}$ [17]. For $Cs_2 NaMn_3F_{12}$ we have found that the solution and refinement of the structure is well possible (R = 0.046) in the pseudo space group $P2_1/m$, the

Table 4

Atomic fractional coordinates and equivalent isotropic temperature factors (A^2) for the triclinic structures of Cs₂NaMn₃F₁₂, Rb₂NaMn₃F₁₂, and Rb₂LiMn₃F₁₂. Corresponding parameters of analogous atoms in each of the three structures are given in that sequence

Atom	r	у	z	U_4
Cs1	0.00860(6)	0.75115(6)	0.88190(4)	0.02860(14)
Rbl	-0.02145(7)	0.73773(7)	0.86141(5)	0.0269(2)
	-0.0125(2)	0.7458(2)	0.86976(12)	0.0274(4)
Cs2	0.48947(6)	0.24360(6)	0.36440(4)	0.02284(13)
Rb2	0.48896(7)	0.25291(7)	0.38995(5)	0.0291(2)
	0.4976(2)	0.2521'2)	0.38745(13)	0.0351(4)
Mal	0.5	0.5	0.0	0.0099(3)
	0.5	0.5	0.0	0.0106(2)
	0.5	0.5	0.0	0.0120(6)
Mn2	0.5	0.0	0.0	0.0102(3)
	0.5	0.0	0.0	0.0108(2)
	0.5	0.0	0.0	0.0130(6)
Mn3	0.0	0.0	0.5	0.0096(3)
	0.0	0.0	0.5	0.0105(2)
	0.0	0.0	0.5	0.0129(6)
Mn4	0.0	0.5	0.5	0.0107(3)
	0.0	0.5	0.5	0.0109(2)
	0.0	0.5	0.5	0.0129(6)
Mn5	0.29115(12)	0.24917(11)	0.72775(8)	0.0109(2)
	0.18943(9)	0.25233(9)	0.78294(6)	0.0116(2)
	0.1999(2)	0.2524(2)	0.7760(2)	0.0134(4)
Na	0.2164(3)	0.7430(3)	0.2516(2)	0.0188(5)
	0.2900(3)	0.7634(3)	0.2545(2)	0.0194(4)
Li"	0.2901(19)	0.7594(24)	0.2572(14)	0.032(6)
Fl	0.4687(5)	0.2317(4)	0.0627(3)	0.0191(8)
	0.5883(4)	0.2322(3)	-0.0142(3)	0.0205(6)
	0.5947(8)	0.2359(8)	-0.0070(6)	0.025(2)
F2	0.3898(5)	0.4547(5)	-0.1550(3)	0.0283(9)
	0.2778(4)	0.4446(4)	~0.0807(3)	0.0216(6)
	0.2642(9)	0.4410(8)	-0.0779(6)	0.022(2)
F3	0.3539(5)	0.0584(5)	~0.1663(3)	0.0243(8)
	0.2542(4)	0.0684(4)	~0.1025(3)	0.0230(6)
	0.2438(8)	0.0716(8)	-0.0985(6)	0.022(2)
F4	0.2079(5)	0.0577(4)	0.5907(3)	0.0201(8)
	0.0560(5)	0.0558(4)	0.6714(3)	0.0292(7)
	0.1279(10)	0.0357(9)	0.6538(6)	0.032(2)
F5	0.0880(5)	0.7330(4)	0.5006(3)	0.0226(8)
	-0.0518(4)	0.7315(3)	0.5649(3)	0.0188(6)
	- 0.050 2(9)	0.7314(8)	0.5652(6)	0.0204(15)
F6	0.2279(5)	0.4278(4)	0.6119(3)	0.0214(8)
	0.1228(5)	0.4462(4)	0.6776(3)	0.0293(7)
	0.1599(9)	0.4503(9)	0.6658(6)	0.027(2)
F7	0.2772(5)	0.5463(5)	0.0761(3)	0.0262(9)
	0.3807(4)	0.4650(4)	0.1604(3)	0.0214(6)
	0.3817(9)	0.4640(9)	0.1606(6)	0.025(2)
F8	0.2840(4)	-0.0608(4)	0.0811(3)	0.0192(8)
	0.3687(4)	0.0497(4)	0.1554(3)	0.0200(6)
	0.3656(9)	0.0420(9)	0.1546(6)	0.028(2)
F9	0.1317(5)	0.0263(4)	0.3455(3)	0.0211(8)
	0.2453(4)	-0.0478(4)	0.4551(3)	0.0248(6)
	0.2302(8)	-0.0556(9)	0.5824(7)	0.029(2)

same as given for the Al compounds. However, the resulting coordination geometry of the Mn(III) centres is again that of compressed octahedra with symmetrical Mn-F-Mn bridges. This unusual Jahn-Teller distortion accompanied by anomalous thermal ellipsoids at the bridging fluorine ligands and, especially, the weak but significant breaking of the monoclinic Laue symmetry (R_{int} (monocl.) = 0.112, R_{int} (tricl.) = 0.024) gave rise to the selection of the triclinic space group *P*I. Now the refinement of a structural model with asymmetrical bridges converged very well at R = 0.028 ($wR_0 = 0.050$).

Very similar triclinic structures have also been found for $Rb_2NaMn_3F_{12}$ and $Rb_2LiMn_3F_{12}$. Like in the Cs_2Li compound, in $Rb_2LiMn_3F_{12}$ the octahedral positions show a small disorder effect: 4% of the Li sites are occupied by Mn and vice versa. The atomic parameters are summarized for all three isostructural compounds in Table 4; the geometrical data are in Table 5.

In spite of the larger asymmetric unit which now contains five independent Mn atoms, the structures show the same features in principle as the aforementioned thombohedral type. As an example, the layer of $Cs_2NaMn_3F_{12}$ is drawn in Fig. 4. In all cases, the same Jahn-Teller ordering of elongated [MnF₆] octahedra is observed as in $Cs_2LiMn_3F_{12}$. The geometry is surprisingly similar, as will be discussed later in summarizing for all structures.

The main differences are in the surroundings of the alkali metal ions. The Cs ions in Cs₂NaMn₃F₁₃ as well as the Rb ions in the remaining two triclinic structures have a rather distorted C.N. 12 only, instead of 18 in the Cs₂Li analogue. The Li ion in Rb₂LiMn₃F₁₂ is now in a distorted 6+1 coordination similar to the Na ions in the Cs₂Na compound, whereas a clear C.N. 7 is achieved in Rb₂NaMn₃F₁₂. One of the Li-F distances is a surprisingly short 1.89 Å, in the region of values for tetrahedrally coordinated Li^{*} like in the garnet Li₃Na₃Fe₂F₁₂ (1.850 Å [20]) or in Li₃VF₆ (1.840–1.909 Å [21]). However, the remaining Li-F distances are rather large (Table 5) so that the average for the first six bond lengths is 2.29 Å, which is much larger than expected for six-coordinated Li.

3.3. Monoclinic structure of Cs₂KMn₃F₁₂

For the Cs_2K compound a monoclinic C-centred unit cell has been found with the following relations of the lattice constants (m) to that of the rhombohedral parent structure in the hexagonal setting (h):

$$a_m \sim -2a_k - b_k; b_m \sim b_k; c_m \sim 2/3a_k + 1/3b_k - 2/3c_k$$

The structure was solved in the space group C2/c (for crystal data and experimental conditions see

Table 4. Continued

Atom	x	у	2	Ueg
F10	0.1380(5)	0.4612(5)	0.3530(3)	0.0214(8)
	0.2297(4)	0.5678(4)	0.4317(3)	0.0218(6
	0.2266(8)	0.5760(8)	0.4174(6)	0.022(2)
F11	0.5180(4)	0.2368(5)	0.6494(3)	0.0244(9)
	0.4088(4)	0.2306(4)	0.6868(3)	0.0260(7
	0.4443(9)	0.2370(10)	0.7030(6)	0.029(2)
F12	0.0716(5)	0.2636(5)	0.8124(3)	0.0256(9)
	-0.0379(4)	0.2737(5)	0.8707(3)	0.0281(7
	-0.0519(8)	0.2600(9)	0.8344(6)	0.027(2)

 U_{eq} is one-third of the trace of the orthogonalized U_{ij} tensor. ⁴ Occupied by 4% Mn, the lacking Li amount is supposed to be distributed on the Mn sites (not considered in the calculations).

Table 5 Selected interatomic distances (λ) and angles (deg) in the triclinic $A_2A'Mn_3F_{12}$ compounds

	Cs2NaMn3F12	Rb ₂ NaMn ₃ F ₁₂	Rb ₂ LiMn ₃ F ₁₂
Mn1-Fl	2×2.126(3)	2.097(3)	2.084(6)
Mini - F2	2×1.864(3)	1.875(3)	1.894(6)
Mn1-F7	2×1.809(3)	1.811(3)	1.809(6)
Mn2-F3	2×2.115(3)	2.147(3)	2.140(6)
Mn2-F1	2×1.869(3)	1.855(3)	1.878(6)
Mn2-F8	2×1.812(3)	1.822(3)	1.819(6)
Mn3-F5	2×2.105(3)	2.142(3)	2.140(6)
Mn3-F4	2×1.875(3)	1.859(3)	1.878(6)
Mn3-F9	2×1.812(3)	1.810(3)	1.819(6)
Mn4F6	2×2.142(3)	2.089(3)	2.093(6)
Mn4-F5	2×1.866(3)	1.880(3)	1.888(6)
Mn4-F10	2×1.812(3)	1.812(3)	1.821(6)
Mn5-F2	2.116(3)	2.123(3)	2.124(6)
Mn5-F4	2.134(3)	2.123(3)	2.125(6)
Mn5–F3	1.874(3)	1.874(3)	1.388(6)
Mn5-F6	1.871(3)	1.876(3)	1.879(7)
MnS-F11	1.814(3)	1.797(3)	1.810(6)
Mn5-F12	1.795(4)	1.805(3)	1.806(6)
Na/Li-F12	2.236(4)	2.280(3)	1.932(13)
Na/Li-F11	2.242(4)	2.260(3)	1.892(14)
Na/Li-F8	2.336(4)	2.421(3)	2.39(2)
Na/Li-F7	2.372(4)	2.494(3)	2.50(2)
Na/Li-F10	2.420(4)	2.341(3)	2.15(2)
Na/Li-F9	2.424(4)	2.484(4)	2.18(2)
Na/Li-F5	2.708(4)	-FI 2.541(3)	2.63(2)
Cs/Rb1-F	12×3.128-3.757	2.781-3.543	2.928-3.774
Cs/Rb2-F	12×2.575-3.613	2.904-4.005	2.936-3.973
Ranges of vi	ght' octahedrai ang	ies	
F-Mn1-F	87.5-92.5	87.5-92.5	87.9-92.1
F-Mn2-F	88.0-92.0	88.291.8	87.6-92.4
F-Mn3-F	87.5-92.5	87.4-92.6	87.4-92.6
F-Mn4-F	87.5-92.5	87.3-92.7	87.3-92.7
F-Mn5-F	87.0-97.0	84.5-97.5	84.4-101.8
Bridge angle.	5		
Mn1-F1-Mr	12 140.1(2)	142.3(2)	141.4(3)
Mn1-F2-Mr	15 143.5(2)	137.1(2)	131.5(3)
Mn2-F3-Mr	5 141.4(2)	135.1(2)	131.2(3)
Mn3-F4-Mr	15 139.0(2)	141.9(2)	138.1(4)
Mn3-F5-Mi	14 142.0(2)	136.9(1)	137.0(3)
Mn4 F6 Mi	138,5(2)	140.4(2)	135.7(3)
Average	140.8	139.0	136.0



Fig. 4. Section of the $\{MnF_4\}^{-}$ layer in Cs₂NaMn₃F₁₂ and its orientation to the unit cell.

Table 1). The atomic parameters are given in Table 6, and the geometrical data in Table 7. Now, three independent Mn atoms are in the asymmetric unit, all on symmetry centres (sites 4a-c).

Again, the Jahn-Teller distortion and ordering is very similar to that of the other structures. The coordination of the Cs ions is 12+2 (Table 7), between that of the Cs₂Li (6+12) and that of the Cs₂Na compound (12). This unexpected sequence is probably connected with the different puckering schemes of the Kagomé layers in the different structure variants as discussed below. The K ions adopt a 6+4 coordination, here.

Table σ Atomic fractional coordinates and equivalent isotropic temperature factors (Å²) for Cs₂KMn₃F₁,

	•			
Atom	x	у	z	U _{eq}
Cs	0.30891(7)	0.2175(1)	0.67539(6)	0.0282(3)
к	0.5	-0.2718(5)	0.75	0.0212(8)
Mnl	0.0	0.0	0.5	0.0115(5)
Mn2	0.5	0.0	0.0	0.0115(5)
Mn3	0.25	0.25	0.0	0.0121(5)
F1	0.4485(6)	0.2346(9)	0.4713(7)	0.032(2)
F2	0.2027(6)	0,310(1)	0.8538(6)	0.028(2)
F3	0.3738(6)	0.5543(9)	0.5358(6)	0.025(2)
F4	0.4818(7)	0.028(1)	0.8546(6)	0.032(2)
F5	0.3370(6)	0.075(1)	0.9699(6)	0.028(2)
F6	0.4287(7)	0.465(1)	0.8545(5)	0.029(2)

 U_{en} is one-third of the trace of the orthogonalized U_{u} tensor.

Table 7 Selected interatomic distances (Å) and angles (deg) in Cs.KMn.F.,

Mnl-F4	2×1.793(7)	Mn3-F2	2×1.512(7)
Mn1-F1	2×1.893(7)	Ma3-F5	2×1.866(7)
Mn1-F5	2×2.124(8)	Mn3-F3	2×2.136(7)
Mn2-F6	2. 798(7)	K-F2	2×2.632(8)
Ma2-F3	2×:.397(7)	K-F4	2×2.679(8)
Ma2-F1	2×2.114(7)	K-F6	2×2.719(7)
		Cs-F	12×2.972-3.619
Ennges of 1	right' octubed-		
ral angles		Bridge angles	
F-MnI-F	86.6-93.4	Mn1-F1-Mn2	141.7(4)
F-Mn2-F	86.1-93.9	Mn2-F3-Mn3	139.6(4)
F-Mn3-F	86.4-93.6	Mn3-F5-Mn1	143.0(4)
		Average	141.4

3.4. Influence of the alkali ions on the layer geometry

3.4.1. Jahn-Teller distortion

If the Jahn-Teller distortion is given as the ratio of the bond length along the elongated axis divided by the average of the bond lengths at the remaining two octahedral axes $(r_1/r_s, Table \delta_r, it can be seen that$ there is no systematical change with the alkali ions $<math>A_2A'$. The corresponding values in the quadratic layers (which also show no clear variation) are all a little higher. Thus, the vibronic coupling in the Kagomé net layer seems to be a little weaker than that in a quadratic TIAIF₄-type layer.

3.4.2. Bridge angles Mn-F-Mn

In a strong contrast to the quadratic layer structures $AMnF_4$, where a variation of A from Li to Cs gives a change of bridge angles from 132.7° to 161.9°, only minor variations are observed for the $A_2A'Mn_3F_{12}$ compounds (Table 8). The span of individual bridge angles within one compound is often greater than the differences between the mean values of different compounds. These average Leidge angles vary from 136.0° to 141.4° only; all of them are lower than the ideal angle of a planar Kagomé net layer built from regular octahedra, which is 150°. That means that remarkable puckering of the layers must occur.

3.4.3. Puckering of layers

An impression of the puckering modes in the three structure types of $A_2A'Mn_3F_{12}$ compounds is given in Fig. 5. Two contributions of puckering may be distinguished: that in the arrangement of metal centres only and that resulting from the tilting pattern of the $[MnF_a]$ octahedra.

For the rhombohedral Cs₂Li compound all the Mn atoms of the Kagomé net are coplanar. The same holds for the monoclinic Cs₂K structure. In the triclinic structures the MnS atoms (on a general position) show small deviations from the plane of the other Mn atoms which are all on centres of symmetry. The resulting waving amplitude in the Mn layers increases from Cs,Na over Rb₂Li towards Rb₂Na.

The three different tilting patterns of the octahedral units are represented by schemes in Fig. 6.

In Cs, LiMn, F₁, all three octahedra are tilted, alternating inside (towards the small Li atom) or all outside the triangle (towards the Cs atom). In the Cs₂K structure a more complicated tilting pattern is evident: two Mn atoms of a triangle show lateral tilts and for one octahedron only an inside/outside inclination. This conforms with the much larger size of the K counter ion above or below the triangles. In the layers oriented parallel to the (001) plane at z = 0 and z =0.5 there is an alternating undulation with the waving directions in [110] and the [110] directions respectively. The angle between these two directions is near 60°. A more pronounced undulation is observed in the triclinic phases where the Mn atoms are involved in the waving, too. Here, the layers are parallel to the [101] plane and the propagation of waves is in the [101] direction.

3.4.4. Inter-layer distances

The inter-layer distances D_{i1} in the $A_2A'Mn_3F_{12}$ compounds were obtained by transforming all structurces to a ps udoce'l corresponding to the hexagonal setting of the rhombohedral parent structure and taking 1/3c as D_{i1} values given in Table 8. The distances are interesting from the point of view of inter-layer magnetic coupling; as expected, they follow

Table 8

Comparison of $A_2A'Mn_3F_{12}$ compounds (ordered with regard to the radii ratio $r_A/r_{A'}$) and AMnF₄ structures [6]: Jaha-Teller distortion $V_{17} = \langle Mn - F \rangle_{boat} / \langle Mn - F \rangle_{boat}$, bridge angles (deg) and inter-layer distances D_A (Å)

Compound	r _A /r _A	Space group	V _n	(Mn-F-Mn)	Da
Cs.LiMn,F.,	2.47	RĪ	1.165	137.9	5.756
Rb.LiMn.F.	2.26	РĪ	1.146	136.0	5.705
Cs.NeMn.F.	1.84	PĪ	1.152	140.6	5.969
Rb.NaMn.F.	1.69	РĪ	1.153	139.0	5.821
Cs,KMn,F12	1.36	C2/c	1.153	141.4	6.000
$AMnF_{+}(A = Li-Cs)$			1.169-1.181	132.7-161.9	4.97-6.64



Fig. 5. Side view of the layers in (a) $Cs_2LiMn_3F_{12}$ from the [110] direction, (b) $Rb_2LiMn_3F_{12}$ from [010] (c) $Cs_5KMn_3F_{12}$ from [001]. Isolated spheres: large A, small A' in $A_2A'Mn_3F_{12}$.



Fig. 6. Octahedral tilting schemes for $Cs_2LiMn_3F_{12}$ (top), the triclinic phases (middle), and $Cs_2KMn_3F_{12}$ (bottom). The arrows give the inclination directions of the octahedral tops.

the size of the smaller A' ion connecting the Kagomé layers, but the larger A ion has an additional effect.

4. Magnetic investigations

Two compounds, triclinic $Cs_2NaMn_3F_{12}$ and monoclinic $Cs_2KMn_3F_{12}$, were investigated with the aid of a SQUID magnetometer in the temperature range between 2 and 300 K. The Li compounds were not



Fig. 7. Reciprocal magnetic susceptibilities versus temperature for (a) $Cs_2NaMn_3F_{12}$ and (b) $Cs_2KMn_3F_{12}$.

considered owing to complications from the observed Li/Mn disorder.

For both compounds the temperature dependence of the reciprocal susceptibilities (Fig. 7) shows a large range of Curic-Weiss behaviour with $\Theta_{\rm p} = -30$ K in both cases. Below about 12 K for the Cs₂Na and 16 K for the Cs₂K compound a field dependence of the magnetization is observed. This effect has been evaluated by measuring at different fields between 0 and 45 kOe; 'true' antiferromagnetic susceptibilities were derived for the low temperature range by extrapolation to H = 0 Oe. These corrected values are given in Fig. 8.

Surprisingly, both the curves for $Cs_2NaMn_3F_{12}$ and $Cs_2KMn_3F_{12}$ behave quite differently at low temperatures. The latter shows a broad maximum at about 15 K indicating 'normal' low-dimensional antiferromagnetic behaviour and at about 7 K a sharp minimum, probably due to 3D ordering. In spite of a very similar shape of the susceptibility curve at higher temperatures, for $Cs_2NaMn_3F_{12}$ no indication for 2D or 3D ordering can be found.

For calculation of the reciprocal susceptibilities (solid lines in Fig. 8) the approximation of Rushbrook and Wood [22,23] for a planar Heisenberg model with S = 2 and fixed g = 2.0 was used with coefficients C_n of Lines [24].

As can be seen in Fig. 8, for $Cs_2KMn_3F_{12}$ a quite good fit of theoretical and experimental data is obtained for an exchange energy J/k = -2.5 K. The amount is higher than the corresponding exchange energies in the AMnF₄ layer compounds (J/k = -1.2 up to +1.3 K).

For Cs₂NaMn₃F₁₂ the susceptibility curve looks like that of a paramagnet but the χ_M values are much too low for an S = 2 paramagnet, as may be seen by comparing with the theoretical curves for the low exchange energies J/k = -1.0 K and -0.1 K included in Fig. 8. Thus, the short range exchange energy must be in the same order of -2.5 K as for the Cs₂K



Fig. 8. Corrected magnetic susceptibilities for Cs₃NaMn₃F₁₂ and Cs₂KMn₃F₁₂ and calculated curves for different exchange energies.

compound, but the lack of a maximum in the susceptibility curve indicates that there is no real 2D or 3D ordering. This unusual behaviour will be investigated further by neutron diffraction and other experiments.

4.1. Exchange interactions in the Kagomé net layers

For the A,MnF_c(H₂O) linear chain compounds [4] and for the AMnF_a compounds with quadratic layer structures [7] the strong influence of the bridge angle β (Mn-F-Mn) on the exchange energies has been demonstrated. For the latter structures with antiferrodistortive Jahn-Teller ordering the influence of possible exchange pathways has been discussed [7,25]. In the $A_2A'Mn_3F_{12}$ layer compounds similar asymmetrical bridges are present. Thus, it is supposed that the same mechanisms will be active. According to qualitative considerations following the Anderson-Kanamori-Goodenough concept [26] and to theoretical calculations by Atanasov [27] using angular overlap and extended Llückel methods, two competing main contributions to the exchange integral can be assumed: a σ/σ^* interaction (left in Scheme 1) and a π/σ interaction (right in Scheme 1).

The former is strongest at bridge angles β near 180° and gives ferromagnetic coupling: the latter is strongest at a hypothetical 90° bridge angle and provides antiferromagnetic coupling. Both mechanisms are enhanced by contributions of 4s/3d mixing which is assumed to play an important role for stabilization of the Jahn-Teller elongation with respect to the alternative compression of octahedra. Indeed, for the AMnF₄ compounds above $\beta = 150^{\circ}$ ferromagnetism had been found (CsMnF₄), below 150° antiferromagnetism. The exchange energies show a linear dependence with cos² β for the layer compounds as well as 10⁴ the alternative com-

Looking at these findings, for both $Cs_2NaMn_3F_{12}$ and $Cs_2KMn_3F_{12}$ with asymmetrical bridges and Mn-F-Mn angles β of 140.6° or 141.4° respectively, dominant antiferromagnetic coupling can be assumed in agreement with the experimental results. The exchange energy of -2.5 K obtained for the Cs₂K compound is remarkably higher than that of AMnF₄



 $\beta = 138.4^\circ$, J/k = -1.15 K; KMnF₄: $\beta = 140.6^\circ/146.4^\circ$, J/k = -0.6 K). A possible reason may be the weaker Jahn-Teller coupling in the Kagomé-type layers. In this way the σ/σ^* interaction may be weakened as the character of d orbitals involved in the asymmetrical bridge (d_2^{12} and $d_{x^2-y^3}^{0}$) becomes blurred. Another influence, which is difficult to estimate, may arise from differences in octahedral tilting patterns, by which mainly π -contributions may be inferred.

compounds with comparable bridge angles (NaMnF₄:

4.2. Magnetic ordering

Now the question arises of a possible magnetic ordering of the antiferromagnetically coupled Mn¹¹¹ centres at low temperatures. Here we deal with the problem of contradictory interactions in a triangular system with antiferromagnetic coupling, often cited under the term 'magnetic frustration'.

Recent theoretical calculations [28] for an isotropic Heisenberg antiferromagnet on a Kagomé lattice yielded disorder of spins even at T = 0 K if exchange only is taken into account. However, the inclusion of dipole-dipole interactions which become more important in anisotropic 2D systems enhances a possible long-range order.

Experimental work on compounds with triangular octahedral structural units has been performed for instance with pyrochlore-related fluorides like CsNiFeF₆ [29] or CsCu₂F₅ [30]. The results of magnetic investigations were interpreted in terms of the spin-glass theory [31]. However, in similar systems, ordered non-collinear spin systems, e.g. with 120° arrangements, have been found (e.g. KMnFeF, [32], KCrF₄ [33]) and are discussed under the term of "start further in the seems possible that both shortrange and long-range ordering modes are realized in our compounds Cs₂NaMn₃F₁₂ and Cs₂KMn₃F₁₂ respectively. Apparently, the small differences in the geometry of the layers either allow for magnetic ordering or do not. Further investigations, e.g. by a.c. susceptometry or neutron diffraction, are necessary to clear up these questions.

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