JOURNAL OF
Materials
CHEMISTRY

Structural investigations of new copper fluorides $NaRECu_2F_8$ ($RE^{3+} = Sm^{3+}, Eu^{3+}, Gd^{3+}, Y^{3+}, Er^{3+}, Yb^{3+}$)

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Received 22nd April 1998, Accepted 30th June 1998

A series of copper(II) and rare earth fluorides has been prepared. The crystal structure of $NaGdCu_2F_8$ has been solved from single crystal data and refined to conventional $R = 0.028$ ($wR = 0.048$) for 585 independent reflections. The symmetry is tetragonal (space group $I422$) with $a = 5.407(1)$ and $c = 10.382(1)$ Å ($Z = 2$). A Rietveld analysis of $NaYCu_2F_8$ and refinements of the powder X-ray diffraction data for the other compounds of the series confirmed the $I422$ space group. The structure consists of layers of CuF_4 square-planes perpendicular to the c-axis, interleaved alternatively by Na^+ or RE^{3+} cations located in antiprisms.

Introduction

During recent years a wide range of ternary fluorides with general formula $A^IM^{III}F_4$ or $A^{II}M^{II}F_4$ have been isolated: their investigation has led to the characterization of various structural types given in ref. 1 and 2 (and references cited therein). When M is a d-transition element, the $KBrF_4$-type[3–5] is often found in the presence of Jahn–Teller M^{2+} or M^{3+} cations. This is particularly true for $CaCuF_4$ which exhibits a tetragonal symmetry[6,7] (space group $I4/mcm$). This structure is related to the fluorite-type by cationic ordering, yielding a doubling of the c parameter value. The whole of the cations shows a fcc stacking, but an important shift of the anionic sublattice leads to define two types of environment for the cations: MF_4 square-planes at $z = 0$ and 1/2 which are isolated one from another. Each layer of $(MF_4)^{2-}$ polyhedra are shifted relative to the other ones and the larger cations A are located between these layers at the center of AF_8 antiprisms.

Some studies devoted to quaternary fluorides belonging to the scheelite family[8,9] have shown that it was possible to substitute the M^{2+}–M^{4+} couple for trivalent ions in $LiREF_4$. In view of these results, it seemed worthwhile to investigate appropriate substitutions in ternary fluorides belonging to the $KBrF_4$-type, which could induce a cationic ordering in eight-fold coordination.

The present paper reports the structural determination of several quaternary $NaRECu_2F_8$ fluorides.

Experimental

Preparation of the compounds

Polycrystalline samples were synthesized by solid state reactions from stoichiometric mixtures of the binary fluorides. The starting materials were mixed under a dry argon atmosphere in a glove box due to oxygen and moisture sensitivity. The reactions were carried out in sealed platinum tubes for 15 h at 550 °C. The reaction mixture was annealed several times in the same conditions with intermediate grindings in order to obtain pure powders. All reactions were followed by a temperature quenching.

X-Ray diffraction analysis

Single crystals were obtained by melting about 2 g of $NaGdCu_2F_8$ at 700 °C followed by cooling to room temperature at a rate of 3 °C h^{-1}.

Weissenberg and precession photographs of a single crystal showed a tetragonal symmetry belonging to the Laue class $4/mmm$ with systematic extinctions $h + k + l = 2n + 1$, consistent with space groups $I422$, $I4mm$, $I\bar{4}2m$, $I\bar{4}m2$, $I4/mmm$.

Intensity data were collected on an Enraf Nonius CAD4 four-circle automatic diffractometer using graphite-monochromated Mo-Kα radiation. Corrections were applied for Lorentz and polarization effects, followed by an empirical absorption correction using ψ-scan technique. For extinction corrections an empirical coefficient ε was used in the expression $F_c(\text{corr}) = F_c\,(1 + 10^{-3}\,\varepsilon F_c^2\,\lambda^3/\sin 2\theta)$. Intensity treatment and refinement calculations were performed using the SHELXL93 program.[10] Atomic scattering factors and anomalous dispersion parameters were taken from ref. 11. Crystal data and experimental conditions are listed in Table 1. The quality of the acquisition and refinement was based on the conventional reliability factors R_{int} and R_1, wR_2 respectively.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/108.

Complementary studies of $NaGdCu_2F_8$ and $NaYCu_2F_8$ phases were carried out by the Rietveld method.[12] Powder X-ray diffraction (XRD) profiles were recorded on a Philips PW

Table 1 Crystal data and experimental conditions for data collection

formula	$NaGdCu_2F_8$
symmetry	tetragonal
space group	$I422$ (no. 97)
unit-cell parameters/Å	$a = 5.407(1)$ $c = 10.382(1)$
volume/Å^3	303.5(1)
Z	2
D_c/g cm^{-3}	5.03
crystal size/mm	0.19 × 0.14 × 0.21
radiation	Mo-Kα ($\lambda = 0.71073$ Å), graphite monochromator
absorption coefficient, μ/mm^{-1}	18.0
$F(000)$	410
measuring range/degrees	$\theta_{max} = 45$
scan type	ω–2θ
index ranges	$-10 \leqslant h \leqslant 10$, $-10 \leqslant k \leqslant 10$, $0 \leqslant l \leqslant 20$
reflections collected	2578
independent reflections	636 [585 $F_o^2 > 2\sigma(F_o^2)$]
extinction coefficient, ε	0.06723
R_{int}	0.0826
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0279$; $wR_2 = 0.0484$
goodness of fit, S	1.201
final Fourier residuals/eÅ^{-3}	-1.57, 1.33

Table 2 Rietveld data and experimental conditions for data collection

formula	$NaGdCu_2F_8$	$NaYCu_2F_8$
symmetry	tetragonal	tetragonal
space group	$I422$ (no. 97)	$I422$ (no. 97)
unit-cell parameters/Å	$a=5.408(1)$	$a=5.370(1)$
	$c=10.390(1)$	$c=10.291(1)$
volume/Å^3	303.9(1)	296.8(1)
Z	2	2
D_c/g cm^{-3}	5.02	4.37
radiation	Cu-Kα ($\lambda=1.5418$ Å), graphite monochromator	
peak shape function $PV=\eta L+(1-\eta)G$	$\eta=0.58$	$\eta=0.25$
FWHM function	$H^2=U\tan^2\theta+V\tan\theta+W$	
measuring range/degrees	$15<2\theta<100$	$16<2\theta<100$
reflections collected	126	126
parameters used in refinement	29	24
cR_p	0.190	0.152
cR_{wp}	0.150	0.118
R_I	0.042	0.038

1050 diffractometer in Bragg–Brentano geometry, using graphite-monochromated Cu-Kα radiation. The sample was set into an air-tight cell, filled in a dry atmosphere, by dusting the powder through a 20 µm sieve in order to minimize orientation effects. Owing to the Bragg–Brentano geometry of the equipment, the mylar windows of the cylindrical cell are crossed by the X-ray beam over a quasi-constant thickness. Data were collected over $15\leqslant 2\theta\leqslant 100°$, in 0.02° steps, with integration times of 20 s.

The refinements were performed with the FULLPROF program package.[13] The background level was optimized with a polynomial function and the peak shape was fitted by a pseudo-Voigt function. The change in the peak full-width at half-maximum (FWHM) across the diffraction pattern was defined by the function determined by Caglioti *et al.*[14] The reliability factors were the usual ones in Rietveld method (R_I, R_p and R_{wp}).[15] The powder data and experimental conditions are given in Table 2.

Structural determination

$NaGdCu_2F_8$

First, the structure was solved in the $I4/mmm$ space group, by conventional Patterson method for the gadolinium and copper atoms positions; sodium and fluorine atoms were located from a difference-Fourier synthesis. The results were in good agreement with a previous structural hypothesis concerning $NaEuCu_2F_8$.[16] The refinement led to $R_1=0.0341$ and $wR_2=0.0786$ with anisotropic atomic displacements, but required to take into account a random distribution of fluorine atoms around copper, the site (32o) being 50% occupied. Secondly, calculations were carried out in the other space groups; the best residual R values were obtained for the $I422$ space group if considering a twinned single crystal ($R_1=0.0279$, $wR_2=0.0484$ with anisotropic thermal factors). The value of Flack's index[17] equal to 0.5 for the refinement in the $I422$ space group could reveal the occurrence of a twin in our crystal; a and b-axes inversion (50%) brought the value of Flack's index close to zero and could explain the results obtained in the $I4/mmm$ space group. Furthermore the refined atomic displacements U considering the $I4/mmm$ space group or the hypothesis of a twinned single crystal with the $I422$ space group have been compared for each element (see Table 3). As far as the $I4/mmm$ hypothesis is concerned, owing to the results found for Gd and F atoms, the U_{eq} value of Na atoms appeared too large whereas that of Cu atoms was too small. The refinement in the $I422$ space group gives more suitable U_{eq} values.

Table 3 Comparison of refined isotropic atomic displacements (Å^2) in $NaGdCu_2F_8$

Atom	U_{eq} ($I4/mmm$)		U_{eq} ($I422$) twinned single crystal	
Gd	(2a)	0.0063(2)	(2a)	0.0066(1)
Na	(2b)	**0.0231(11)**	(2b)	0.0107(5)
Cu	(4d)	**0.0023(2)**	(4d)	0.0099(1)
F	(32o)	0.0163(7)	(16k)	0.0161(4)

According to the crystallographic data, $NaGdCu_2F_8$ crystallizes in the $I422$ space group with unit-cell parameters $a=5.407$ and $c=10.382$ Å. The final values of atomic coordinates and anisotropic atomic displacements are listed in Table 4. Table 5 gives the main interatomic distances and angles. The bond lengths obtained are close to the sum of the Shannon radii[18] (for Na^+ and Gd^{3+} with C.N.$=8$ and for Cu^{2+} with C.N.$=4$; in each case F^- is threefold coordinated to cations as in $CaCuF_4$).

In addition, piezoelectric measurements were carried out in order to show the occurrence of a non-centrosymmetrical group. Confirmation of the postulated space group was not possible using this technique.

Finally, a powder diffraction study seemed necessary to avoid the twinning effect observed in the single-crystal investigation. The structure of $NaGdCu_2F_8$ was refined by the Rietveld method.[12] However, during the synthesis it was impossible to avoid traces of hexagonal $NaGdF_4$;[19] this phase has been taken into account in the refinement on the basis of the structural hypothesis of $NaNdF_4$.[20] One should note that the R_I factor relating to this impurity remains high (*ca.* 30%) owing to its rather small quantity. Moreover the peaks of $NaGdF_4$ are not well separated from the main diffraction lines of the new compound. The $I422$ and $I4/mmm$ space groups were tested, following exactly the same procedure. The comparison of the reliability factors and of the isotropic thermal displacements showed that the best results were obtained with $I422$ space group (Table 6). In addition, the negative value of B_{iso} found for the sodium led us to assume a small exchange between Gd^{3+} and Na^+ ions in the 2a and 2b sites respectively. As is shown in Table 6, the best refinement corresponds to an exchange rate equal to 3.5%. This is consistent with the similarity between both these sites. Nevertheless such a result was not observed in the single crystal study. It could be explained considering the mode of cooling in each case : the single crystal was subjected to a very slow cooling which favours a complete ordering, whereas the powder was cooled by a temperature quenching which could generate an exchange between two similar sites. However this exchange rate of 3.5% has been tested for the single crystal, and the results of refinement are quite acceptable. Thus, the structural parameters of powder XRD are in good agreement with the crystal study, and the reduced coordinates correspond as near as one and the half standard deviation.

Moreover the best argument in favour of $I422$ space group was the determination of the structure factors for the (211) and (213) reticular planes. Indeed the intensity of the XRD lines according to the Debye law $[F(hkl)=A+iB]^{21}$ with $h\neq k\neq 0$ and $l\neq 0$ differs strongly depending on the space group: the centrosymmetric space group $I4/mmm$ leads to $B=0$ whereas in the $I422$ space group B differs from 0. The comparison of X-ray diffraction patterns for both hypotheses in Fig. 1 and the values of structure factors in Table 7 showed clearly these differences and a best fit in $I422$ space group.

Finally the powder diffraction study confirms the single crystal structure determination and one can conclude that $NaGdCu_2F_8$ crystallizes in the $I422$ space group. In order to verify if all the compounds of the $NaRECu_2F_8$ series exhibit exactly the same structure, another phase involving a smaller rare earth ion such as Y^{3+} was studied by powder XRD.

Table 4 Atomic coordinates and displacements (Å^2) in $NaGdCu_2F_8$ [estimated standard deviations (esds) in parentheses]

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Gd	2a	0	0	0	0.0065(1)	0.0065(1)	0.0069(2)	0	0	0	0.0066(1)
Na	2b	0	0	0.5	0.0102(7)	0.0102(7)	0.0116(11)	0	0	0	0.0107(5)
Cu	4d	0	0.5	0.25	0.0099(2)	0.0099(2)	0.0097(2)	0	0	0	0.0099(1)
F	16k	0.1872(5)	0.3303(5)	0.3763(2)	0.0158(8)	0.0132(8)	0.0191(10)	0.0025(6)	−0.0083(7)	−0.0018(9)	0.0160(4)

Table 5 Interatomic distances (Å) and angles (°) in $NaGdCu_2F_8$ (esds in parentheses)

	(4×) 1.893(2)				
Cu−F	(4×) 2.785(2)	Gd−F	(8×) 2.314(2)	Na−F	(8×) 2.422(2)
F−Cu−F	87.81(13)	F−Gd−F	72.05(4)	F−Na−F	70.42(8)
	92.34(13)		74.24(9)		73.66(4)
	175.95(13)		86.02(12)		84.93(11)
			112.56(9)		115.94(8)
			133.29(13)		130.61(12)
			152.61(13)		153.85(13)

Table 6 Isotropic thermal displacements for different structural hypotheses and corresponding R factors for $NaGdCu_2F_8$ (esds multiplied by Berar's factor in parentheses)

	B_{iso}/Å^2						
Space group	2a	2b	4d	32o/16k	R_I	cR_p	cR_{wp}
$I4/mmm$	0.07(16)	0.9(9)	0.9(3)	2.4(7)	0.070	0.214	0.176
$I422$ without exchange	0.50(13)	−1.6(5)	0.6(2)	1.2(3)	0.044	0.195	0.154
$I422$ with exchange 96.5%/3.5%	0.31(12)	0.5(6)	0.9(2)	1.4(3)	0.042	0.190	0.150

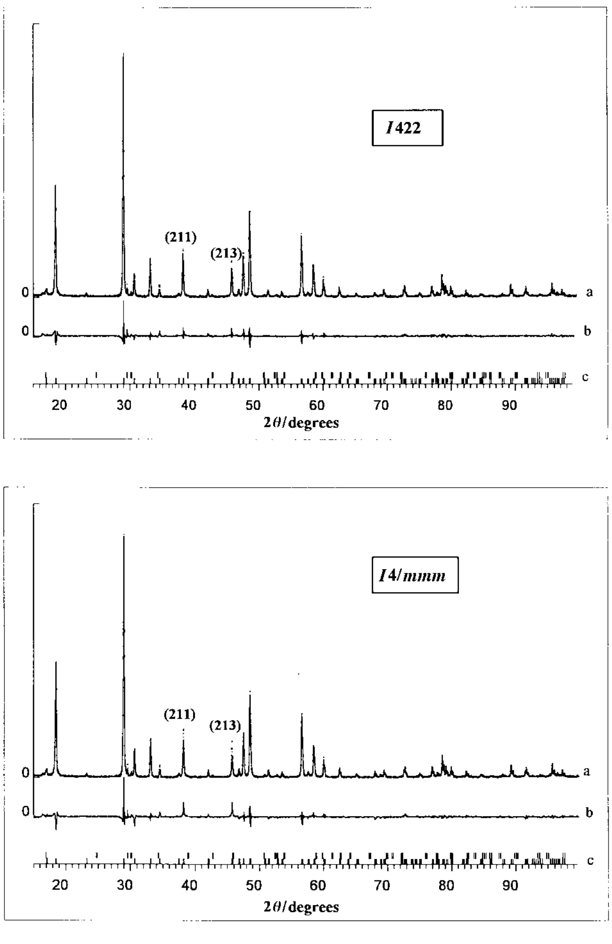

Fig. 1 X-Ray diffraction patterns of $NaGdCu_2F_8$: (a) observed (···), calculated (——) and (b) difference; the tick marks labelled (c) represent the position of the diffraction lines for $NaGdF_4$ (top) and for $NaGdCu_2F_8$ (bottom).

Table 7 Comparison of the observed and calculated structural factors in arbitrary units for the two reticular planes (211) and (213) in the case of the single crystal study

	$F(hkl)=A+iB$					
	$I422$		$I422$ with twinned single crystal		$I4/mmm$	
hkl	F_o	F_c	F_o	F_c	F_o	F_c
211	8691	8690	8663	8684	8046	6466
213	9127	9230	9104	9254	8581	7244

$NaYCu_2F_8$

The structure of $NaYCu_2F_8$ was refined by the Rietveld method. The previous structural results of $NaGdCu_2F_8$ were used as a starting model.

The $I422$ and $I4/mmm$ space groups were considered as structural hypothesis; we did not succeed in obtaining good results with the latter ($cR_p=0.200$, $cR_{wp}=0.184$, $R_I=0.0875$). On the contrary, the refinement in the $I422$ space group rapidly converged to $cR_p=0.162$, $cR_{wp}=0.127$ and $R_I=0.050$. A negative thermal displacement on the sodium site and a large one on the yttrium site led us to consider an exchange rate of 8% between Y^{3+} and Na^+ ions in the 2a and 2b sites respectively ($cR_p=0.152$, $cR_{wp}=0.118$, $R_I=0.038$). The refined atomic coordinates and isotropic thermal displacements are listed in Table 8. The main interatomic distances and angles are given

Table 8 Atomic coordinates and isotropic thermal displacements (Å^2) in $NaYCu_2F_8$ (esds multiplied by Berar's factor in parentheses)

Atom	Site	x	y	z	B_{iso}	Occupancy (%)
Y	2a	0	0	0	0.6(2)	92
Na	2a	0	0	0	0.6(2)	8
Y	2b	0	0	0.5	1.1(7)	8
Na	2b	0	0	0.5	1.1(7)	92
Cu	4d	0	0.5	0.25	1.0(2)	100
F	16k	0.1897(14)	0.3332(14)	0.3775(12)	1.2(3)	100

Table 9 Interatomic distances (Å) and angles (°) in $NaYCu_2F_8$ (esds multiplied by Berar's factor in parentheses)

Cu—F	(4×) 1.887(10) (4×) 2.775(9)	Y—F	(8×) 2.274(9)	Na—F	(8×) 2.414(9)
F—Cu—F	88.3(8)	F—Y—F	72.1(4)	F—Na—F	69.4(5)
	91.9(6)		74.3(6)		74.2(4)
	174.7(9)		85.7(6)		84.3(6)
			112.6(5)		117.0(5)
			133.6(7)		130.1(6)
			152.2(7)		153.9(7)

Table 10 Unit-cell parameters of the $NaRECu_2F_8$ series

Compounds	a/Å	c/Å	V/Å^3
$NaSmCu_2F_8$	5.426(1)	10.430(3)	307.1(2)
$NaEuCu_2F_8$	5.412(2)	10.398(2)	304.5(3)
$NaGdCu_2F_8$	5.407(1)	10.382(1)	303.5(1)
$NaErCu_2F_8$	5.360(1)	10.270(2)	295.0(1)
$NaYbCu_2F_8$	5.354(2)	10.225(2)	293.1(3)
$NaYCu_2F_8$	5.370(1)	10.290(1)	296.8(3)

in Table 9. The Na—F and Cu—F bond lengths are of the same order of magnitude as those obtained in $NaGdCu_2F_8$. The Y—F distance is shorter than Gd—F for the same site 2a, in good agreement with the smaller ionic radius of Y^{3+}.[18]

The $NaRECu_2F_8$ series

This series has been studied for several rare earths. As far as the largest rare earth ion is concerned, only the phase containing Sm^{3+} has been isolated when SmF_3 was stabilized in the variety which crystallizes in orthorhombic symmetry. The hexagonal form of SmF_3 did not react with the other binary fluorides to give the quaternary compounds. Therefore the series exists only with rare earth fluorides which adopt the YF_3-type structure (space group *Pnma*).[22] The Lu^{3+} ion is expected to be the lower limit of the series.

The phases containing the cations Sm^{3+}, Eu^{3+}, Gd^{3+}, Er^{3+}, Yb^{3+} and Y^{3+} have been studied. For each compound, the unit-cell parameters have been determined from slow powder diffraction pattern (angle step: 0.02° and counting time: 10 s) using a silicon standard, followed by least-squares refinement. All parameters are listed in Table 10. The unit-cell volume decreases gradually as a function of the rare earth size.

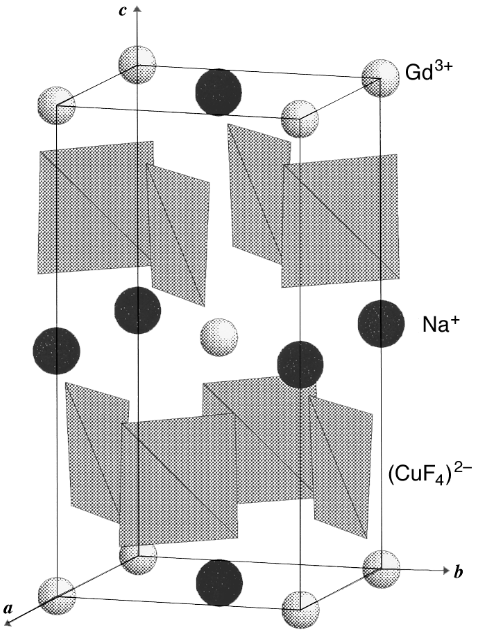

Fig. 2 Perspective view of $NaGdCu_2F_8$ structure.

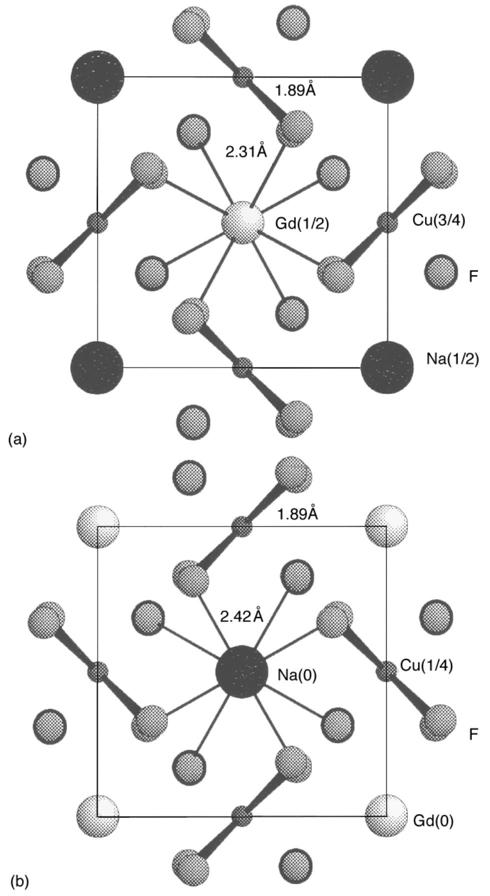

Fig. 3 (001)-projection of $NaGdCu_2F_8$ structure: (a) Gd environment, (b) Na environment (surrounded fluorine atoms are located below the Na or RE atom plane). The respective distances are indicated

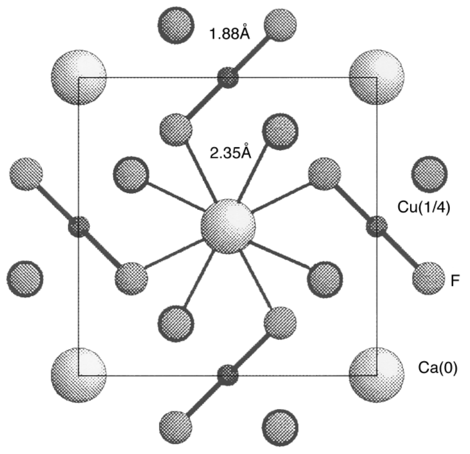

Fig. 4 (001)-projection of $CaCuF_4$ structure (surrounded fluorine atoms are located below the Ca atom plane).

Description of the structure and discussion

The structure of $NaRECu_2F_8$ can be related to that of $CaCuF_4$ (space group *I*4/*mcm*)[6,7] which crystallizes in the $KBrF_4$-type.[5] A perspective view is represented in Fig. 2. Projections of $NaGdCu_2F_8$ and $CaCuF_4$ on the (001) plane are shown in Fig. 3 and 4.

The Ca—F bond length in $CaCuF_4$ is 2.349 Å.[7] Owing to the cationic ordering in $NaGdCu_2F_8$, two distinct Gd—F and Na—F bond distances are found at 2.314 and 2.422 Å, respectively.

In the fluorite-type structure, the Ca^{2+} ions are eight-fold coordinated to fluorine and occupy a site of cubic symmetry. In $NaRECu_2F_8$, the occurrence of Cu^{2+} cations in square planar environment constrains the larger cations (Na^+ and RE^{3+}) to be in more or less distorted tetragonal antiprisms depending on their size and their charge.

The four short Cu—F distances (1.893 Å) are of the same order of magnitude, but slightly longer, than those encountered in $CaCuF_4$ (1.880 Å) and $SrCuF_4$ (1.858 Å).[7] All these structures are constructed from layers of isolated $[CuF_4]^{2-}$ units perpendicular to the *c*-axis and shifted with respect to each other. In each layer a $[CuF_4]^{2-}$ square-plane is oriented at 90° from each adjacent one. The Na^+ and RE^{3+} ions are located between these layers.

In this structure, compared to the *I*4/*mcm* space group of $CaCuF_4$, the disappearance of the sliding plane *c* leads to a small tilting of the $[CuF_4]^{2-}$ square-planes from the bisecting plane $[(a+b)/2,\ c]$ in contrast with $CaCuF_4$, inducing a F—Cu—F angle slightly different from 90° (Table 5, Fig. 3). Such a distortion of the square-planes has already been observed in $KAuF_4$ [5] where it could be due to the strong Jahn–Teller effect of Au^{III} in low-spin state. In the case of $NaRECu_2F_8$, such a tilting must be related to the cationic ordering which takes into account the different size and charge of Na^+ and RE^{3+}.

However the higher ion exchange rate equal to 8% has been found surprisingly for $NaYCu_2F_8$ where the difference of ionic radii between Na^+ and Y^{3+} is the largest. Nevertheless one should notice that in this latter phase the F—Cu—F angle is closer to 90° and consequently the distortion of $[CuF_4]^{2-}$ square-planes is smaller compared to $NaGdCu_2F_8$ compound for instance. Thus the raising of ion exchange rate could be associated with the decreasing of the $[CuF_4]^{2-}$ square-plane distortion, and also are related to the electronic configuration of the rare earth.

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Paper 8/03015D