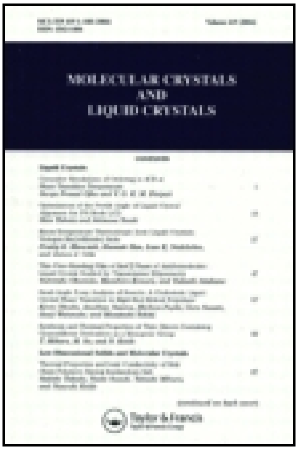

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S. A. Solin [a], D. Mines [a] & R. Haushalter [a]

[a] NEC Research Institute, 4 Independence Way, Princeton, New Jersey, 08540, U.S.A.

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THE SYNTHESIS, STRUCTURE AND INTERCALATION PROPERTIES OF FLUORMICA CLAYS

S.A. SOLIN, D. HINES AND R. HAUSHALTER
NEC Research Institute, 4 Independence Way, Princeton,
New Jersey 08540, U.S.A.

Abstract We show that fluormica clays with compositions close to $Sr_{0.75}Mg_{2.75}(AlSi_3)O_{10}F_2$ may possess a novel two dimensional kagomé magnetic structure when Sr is exchanged for magnetic ions and we report the first synthesis of such a host clay and its magnetic intercalation compounds. The synthesis, structural and intercalation properties of these compounds will be described.

INTRODUCTION

One of the most important problems in magnetism concerns the form of the magnetic ground state in frustrated antiferromagnetically coupled systems. One such system which has been the subject of considerable theoretical interest is the ordered two dimensional (2D) kagomé antiferromagnet.[1] To date the closest physical realization of a 2D kagomé antiferromagnet is $Sr_xCr_{8-x}Ga_{4+x}O_{19}$, SCGO(x).[2] However, this material always contains randomly substituted non magnetic gallium ions on the chromium sites. Thus, although SCGO(x) does exhibit interesting magnetic properties[2] it is not an ordered 2D kagomé antiferromagnet. We show that layered silicate clays of the fluormica type may exhibit this novel magnetic structure and report here the first results on the synthesis, structure and intercalation properties of this new class of layered magnetic compounds.

Beall[3] has synthesized fluormicas with approximate composition $Sr_xMg_{3.5-x}(AlSi_3)O_{10}F_2$, x = 1/2,1 using high temperature synthesis methods. The resultant compounds are structurally very similar to the 2:1 layered alumino-silicate vermiculite.[4] The 2:1 notation signifies that the host layers consist of two tetrahedral silicate sheets sandwiching one octahedral sheet. Central to the tetrahedral layers are silicon or aluminum atoms, tetrahedrally bonded to oxygens. Those oxygens which form the tetrahedral bases border the interlamellar gallery and are arranged in hexagonal rings which form a kagomé lattice. At the geometric mid plane of each alumino-silicate layer reside atoms octahedrally coordinated to these oxygens which comprise the tetrahedron tips. In trioctahedral silicates, all octahedral sites are filled, primarily with Mg^{2+}. Dioctahedral materials have only 2/3 of the octahedral sites filled, usually with Al^{3+}. The vacant octahedral sites of the dioctahedral layer are situated above (or below) the hexagonal pocket in the basal kagomé lattice. The oxygen situated above the hexagonal ring (both structural types) is not shared with the tetrahedral layer. In vermiculite this oxygen is terminated with a proton, resulting in a hydroxyl group above the kagomé ring whereas in fluormicas the hydroxyl group is replaced by a fluorine ion. The net negative charge on the host layer is balanced by the charge on the gallery cations which must be present to ensure overall charge neutrality. In the simplest picture, this cation nests in the hexagonal cavities and is surrounded by the twelve basal oxygens of the bounding host layers.

To illustrate the salient structural features of the fluormicas of interest here we refer to the idealized structure[4,5] depicted in Fig 1. The vertices of the lattice shown in Fig. 1 represent the oxygen atoms on the basal surface of the fluormica layer. This kagomé lattice is unmodifiable in layered silicates. The solid and hatched disks in Fig 1 represent exchangeable gallery cations.

In the Sr^{+2} fluormica with $x=1$ all hexagonal pockets are filled and the host layer has a net unit cell charge of -2

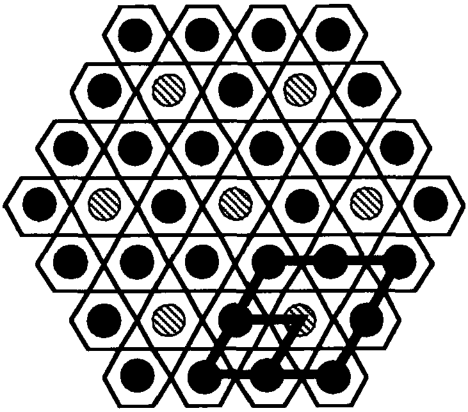

FIGURE 1 A schematic representation of the basal oxygen plane of a fluormica. The kagomé host and super lattice unit cells are shown as heavy solid lines (see text).

yielding overall charge neutrality. With x=1/2, the fluormica layer charge is -1 and only 1/2 of the hexagonal pockets are occupied. Note that for x = 3/4, only 3/4 of the available hexagonal sites in Fig 1 (those denoted by solid disks) will be filled. This is exactly what is required for the gallery cations to form a (2X2)R0° kagomé superlattice of the host layer oxygen kagomé lattice. Thus our experimental strategy is to synthesize Sr fluormicas with x = 3/4 and then exchange the Sr^{2+} ions with magnetic ions such as Ni^{2+}. Direct synthesis of the magnetic fluormicas is not possible because the much smaller magnetic ions select the octahedral intralayer sites and reject the gallery sites in direct synthesis.

SYNTHESIS AND STRUCTURE

Using high temperature (>1400°C) preparation methods similar to those described by Beall[3] we have carried out the first synthesis of the $Sr_{3/4}$ fluormica. Chemical analysis reveals a layered alumino-silicate with the composition $Sr_{0.71}Mg_{2.45}(AlSi_{2.51})O_{8.7}F_2$ (O and F calculated from

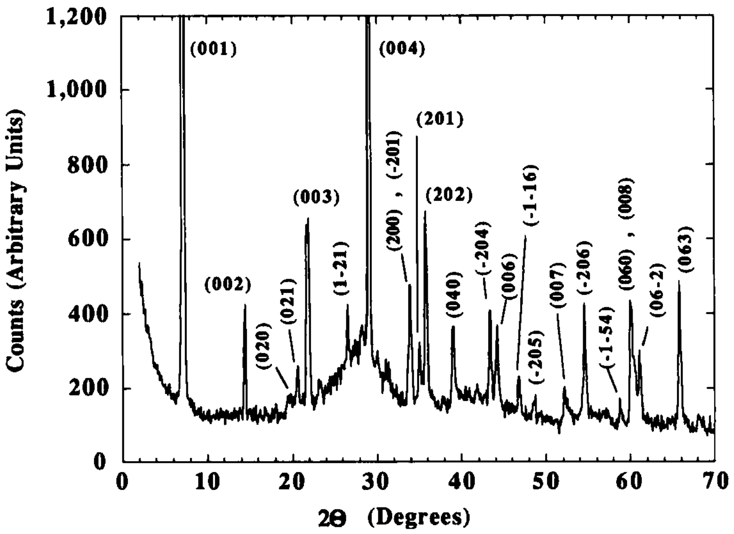

FIGURE 2 X-ray powder pattern of $Sr_{3/4}$ fluormica with 1 water layer excited with Cu kα radiation.

stoichiometry). The X-ray powder pattern of this material indicates a layered clay structure with a basal spacing of 9.708Å. This material readily ingests one layer of water at room temperature. The precession (single crystal) and powder (see FIGURE 2.) X-ray patterns of the hydrated form indicate a triclinic structure with a=5.295Å, b=9.272Å, c=12.312Å, a=93°, β=94.5°and γ=90°. A full structural refinement to determine atomic positions is imminent.

ION EXCHANGE

To promote complete exchange of Sr ions for divalent magnetic ions we employed aqueous solutions of either ethylenediaminetetraacetate (EDTA) or n-butyl ammonium (nBA) to "pry open" the silicate galleries. The former when combined with Li^+ reacted with the host layers but immersion of the pristine $Sr_{3/4}$ clay in an nBA/HCl solution at pH7 caused rapid swelling of the host layer spacing to c=18.43Å.

Intercalation Of The Magnetic Ions

When the resultant nBA intercalated clay is immersed in the chloride salt solutions of Mn, Co, or Ni, and is heated in sealed pressure vessels, the nBA and remaining Sr ions are exchanged with the magnetic species. This exchange is essentially complete with the residual nBA at or below the range of accuracy of the chemical analysis and the remaining Sr at < 5%. The above described hydrothermal ion exchange process also promotes recrystallization of the fluormica platelets so that the crystallite size and quality depend somewhat on the intercalation temperature and the reaction time. For Ni exchange, the optimum parameters were found to be 125^{0}C for 24 hours with a 45 ml reaction vessel containing 1 molar $NiCl_2$ and 100 mg of the nBA fluormica. This yielded some hexagonal platelets as large as 100μm.

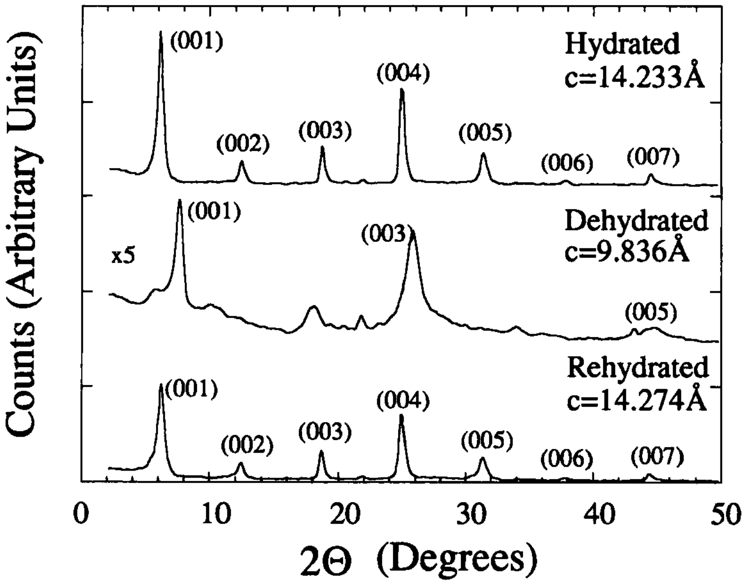

FIGURE 3 The (00*l*) X-ray diffraction patterns of hydrated, dehydrated and rehydrated Ni fluormica containing two water layers in the gallery. The c-axis basal spacings are shown.

HYDRATION-DEHYDRATION

Zhou et.al.[6] have shown that the hydration of magnetic vermiculite intercalation compounds dramatically affects their magnetic properties. Therefore, in preparation for magnetic measurements of the fluormicas we have examined the host layer integrity and basal spacing changes induced by sequential dehydration and rehydration of those compounds. The results for the Ni guest are shown in FIG. 3. The c-axis stacking disorder increases significantly on dehydration but the layer integrity is preserved since the hydrated and rehydrated samples yield similar diffraction patterns.

CONCLUDING REMARKS

While the (2X2)R0° kagomé superlattice appears to be the most symmetric (lowest energy) structure available in the 3/4 filled magnetic fluormicas, it may be kinetically inhibited. Therefore we are actively studying the inplane diffraction properties to confirm the presence of this structure. In parallel with these structural studies, we have carried out temperature and field dependent magnetic susceptibility measurements. Our preliminary results indicate that hydrated $Ni_{3/4}$ fluormica is ferromagnetic (T_C ~24K) while the dehydrated form is a spin-glass (T_C ~4K).

REFERENCES

1. I. Syozi, Prog. Theor. Phys., 6, 306 (1951).
2 A.P. Ramirez, G.P. Espinosa and A.S. Cooper, Phys. Rev. Lett., 64, 2070 (1990).
3. G.H. Beall, in Advances in Nucleation and Crystallization in Glasses, ed. by L.L. Hench and S.W. Freiman, (Am. Ceramic Soc., Columbus, 1971), p.251.
4. G.W. Brindley and G. Brown, Crystal Structures of Clay Minerals and their X-Ray Identification, (Minerological Soc., London, 1980).
5. The actual structure is more complex. See ref. 4.
6. P. Zhou, J. Amarasekara, S. A. Solin, S.D. Mahanti, and T.J. Pinnavaia, Phys. Rev., B15, in press.