Geometric Magnetic Frustration in $Ba_2Sn_2Ga_3ZnCr_7O_{22}$: A Two-Dimensional Spinel Based Kagomé Lattice

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The properties of a two-dimensional geometrically frustrated magnetic material based on the Kagomé net, $Ba_2Sn_2ZnGa_3Cr_7O_{22}$, are reported. The Kagomé net is fully filled with magnetic ions. A Curie-Weiss theta $\theta_W = -312$ K is found with a spin glass transition at approximately 1.5 K, indicating strong geometrical magnetic frustration. This compound is the most two dimensional of a structural series with the geometrically frustrated materials $ZnCr_2O_4$ and $SrCr_8Ga_4O_{19}$. The comparison of their properties tests the influence of different degrees of coupling between Kagomé layers on magnetic frustration within a single chemical and structural family.

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In spite of intensive investigation of the properties of insulating magnetic materials, relatively little is known about compounds for which the long-range magnetic ordering of strongly interacting spins is frustrated by their geometric arrangement in the crystal lattice [1]. Such materials are unique in that they allow the study of a spin system which remains magnetically disordered when cooled well below the ordering temperature expected from the strength of the pairwise spin interaction. Within this paradigm, geometrically frustrated magnetic systems have low-energy states residing on a periodic lattice, unlike the randomly bonded network of glasses. One of the most studied of such compounds is quasi-two-dimensional (2D) $SrCr_8Ga_4O_{19}$ (SCGO) [2]. The local moment derives from the well-understood Cr^{3+} $S = \frac{3}{2}$ ion in an octahedral oxygen cage, and the majority of such moments are arranged on the vertices of a bilayer Kagomé net of corner-sharing triangles, a classic frustrating structure. In the parent compound of the geometrically frustrated chromates, spinel structure $ZnCr_2O_4$ [3], these Kagomé bilayers are fully connected in the third dimension in a tetrahedral arrangement of magnetic sites, also a frustrating geometry. The magnetic lattice of SCGO is derived from the spinel lattice much as the layered Ruddelsden-Popper (RP) 3-2-7 bilayer phase is derived from the perovskite lattice. In the perovskites, the RP series allows for the tuning of interlayer coupling, and has led to better understanding of strongly correlated states in cuprates, manganites, and ruthenates. Here we report the properties of a new geometrically frustrated magnetic compound based on the Kagomé net, $Ba_2Sn_2ZnGa_3Cr_7O_{22}$. This compound, with the "*QS* ferrite" structure type, is fully structurally layered, without the magnetic ions the intermediary layers which are present for SCGO, making it the most 2D compound known in this spinel-based equivalent of the RP series. Comparison of the properties indicates a dramatic increase in frustration on going from the fully coupled spinel to the weakly coupled SCGO lattice, and a subtle change in the manner in which entropy is lost when the weak interlayer coupling in SCGO is weakened further in *QS* ferrite.

The *QS* ferrite structure (Fig. 1) is a member of the large family of ferrites, which are based on the alternation of hexagonal slices of the spinel structure (the "*S*" layer) with other structural components (in this case the "*Q*" layer). The hexagonal spinel layer contains planes of transition metal sites in the Kagomé geometry, a 2D net of corner-sharing triangles. (These Kagomé layers are found in both the ferrites and the jarosites [4,5].) Such a geometric arrangement exhibits both the magnetically frustrating triangular unit, and underconstraint. The underconstraint, is also exhibited in the random atomic network of glasses and accounts for these nets' population of nearly equivalent low-energy states [6].

The *QS* ferrite structure type has been previously reported for a variety of iron-based ferromagnets [7,8]. This phase forms a structural series with two other ferrites, spinel, and magnetoplumbite (the structure of SCGO), in which the distance between neighboring Kagomé planes, and consequently the magnetic coupling between those planes, varies (Fig. 2). Chromium-based spinel and SCGO have been shown to exhibit strong geometrical frustration [1–3,9], but a Cr-based *QS* ferrite was previously unknown. Here we report the characterization of new compounds in which the magnetic Kagomé layers of *QS* ferrite are populated by Cr^{3+}, with no magnetic ions in the intermediate layers. This was accomplished in materials of formula $Ba_2Sn_2ZnGa_3Cr_7O_{22}$ and $Ba_2Sn_2ZnGa_4Cr_6O_{22}$. The compounds were synthesized from stoichiometric mixtures of $BaCO_3$, SnC_2O_4, ZnO, Ga_2O_3, and Cr_2O_3 heated in air in dense Al_2O_3 crucibles at 1350 °C for 36 h, with two intermediate grindings. The samples were then annealed at 900 °C for 7 days to promote cation ordering.

We have determined the crystal structures of the compounds by powder neutron diffraction [10]. The results of

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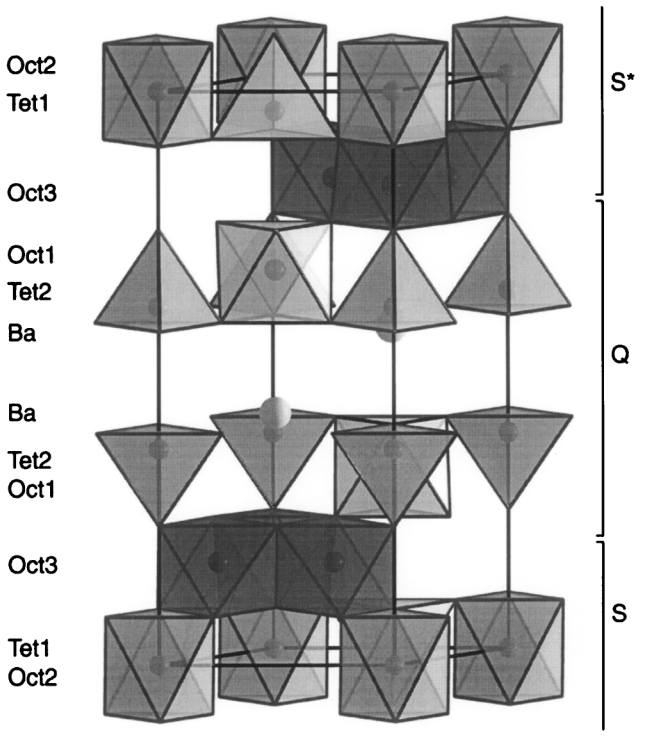

FIG. 1. Crystal structure of the *QS* ferrites $Ba_2Sn_2ZnGa_3Cr_7O_{22}$ and $Ba_2Sn_2ZnGa_4Cr_6O_{22}$, represented as metal-oxygen polyhedra.

the structural refinements are summarized in Table I. The structure has the general formula

$$Ba_2Sn_2^{(Oct1)}[Zn, Ga]_2^{(Tet1)}Ga_2^{(Tet2)}M_1^{(Oct2)}M_6^{(Oct3)}O_{22}\,.$$

Starting (Fig. 1) at the middle of the cell, a double BaO_3 layer is bordered both above and below by a layer which contains Sn^{2+} octahedra (Oct1) and Ga^{3+} tetrahedra (Tet2). This is the "*Q*" type structural unit. There are no magnetic atoms in this layer, so it acts as a large (9.4 Å) spacer between magnetic atom layers. The *Q* block alternates with the spinel-type sandwich layer ("*S*"), which

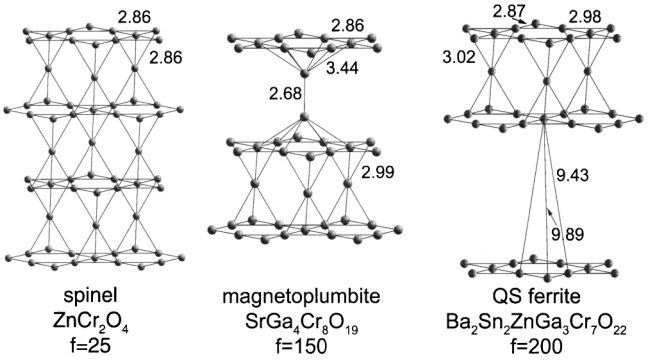

FIG. 2. Magnetic lattices and summary of the magnetic properties of the Kagomé-net materials spinel ($ZnCr_2O_4$), SCGO ($SrCr_8Ga_4O_{19}$), and *QS* ferrite ($Ba_2Sn_2ZnGa_3Cr_7O_{22}$). f is the ratio between the Weiss theta and the spin glass or Neel ordering temperature.

consists of the three characteristic close-packed structural planes of spinel. The *S* block consists of two Kagome geometry layers of metal-oxygen octahedra (Oct3) in the Kagomé geometry separated by a layer of both tetrahedra (Tet1) and octahedra (Oct2). In both *QS* ferrites studied here, the Tet1 site is occupied by a mixture of Ga^{3+} and Zn^{2+}, both of which are nonmagnetic ions, in a 1:1 ratio.

For $Ba_2Sn_2ZnGa_3Cr_7O_{22}$, both the Oct3 and Oct2 sites are fully occupied by Cr^{3+}, with no mixing of any other atoms. The triple-layer sandwich of two Kagomé layers and an enclosed connecting magnetic layer is exactly equivalent to the magnetic lattice which continues infinitely in the third dimension for the spinel $ZnCr_2O_4$. In the present case, the magnetic lattice is confined to 2D by the bordering *Q* layers. The composition $Ba_2Sn_2ZnGa_4Cr_6O_{22}$ was synthesized in an attempt to isolate the Kagomé layers further by putting Cr^{3+} in the Oct3 sites only, with the octahedron in the spinel connecting layer (Oct2) occupied by Ga^{3+} rather than Cr^{3+}. The structure refinements showed, however, that some of the additional Ga^{3+} mixed in on the Kagomé layer, introducing chemical disorder into the magnetic lattice. Thus for $Ba_2Sn_2ZnGa_3Cr_7O_{22}$ the magnetic lattice is fully ordered, with geometry being the only possible source

TABLE I. Structural parameters for $Ba_2Sn_2ZnGa_3Cr_7O_{22}$ (first line) and $Ba_2Sn_2ZnGa_4Cr_6O_{22}$ (second line) at room temperature. Space group: $P6_3/mmc$.

	a = 5.85217(7) Å 5.85510(6) Å		c = 14.2390(2) Å 14.2463(2) Å	
Atom	x	y	z	B (Å^2)
Ba (2*d*)	1/3	2/3	0.4245(3)	0.73(7)
	1/3	2/3	0.4241(5)	0.8(1)
Sn (2*d*)	1/3	2/3	0.6823(3)	0.42(5)
(Oct1)	1/3	2/3	0.6823(4)	0.57(7)
Zn/Ga (2*d*)[a]	1/3	2/3	0.9546(2)	0.44(5)
(Tet1)	1/3	2/3	0.9544(3)	0.41(7)
Ga (2*c*)	0	0	0.3730(2)	0.52(5)
(Tet2)	0	0	0.3735(3)	0.46(7)
Cr/Ga (1*a*)[b]	0	0	0	0.24(4)
(Oct1)	0	0	0	0.50(5)
Cr/Ga (6*i*)[b]	0.1698(3)	−0.1698(3)	0.1695(2)	0.24(4)
(Oct3)	0.1698(5)	−0.1698(5)	0.1701(2)	0.50(5)
O(1) (2*c*)	0	0	0.2390(4)	0.16(6)
	0	0	0.2390(3)	0.56(5)
O(2) (2*d*)	1/3	2/3	0.0920(3)	0.55(7)
	1/3	2/3	0.0918(4)	0.6(1)
O(3) (6*i*)	0.1533(3)	−0.1533(2)	0.9140(2)	0.50(4)
	0.1537(3)	−0.1537(3)	0.9140(2)	0.48(6)
O(4) (6*i*)	0.4939(3)	−0.4939(3)	0.2426(2)	0.66(3)
	0.4938(5)	−0.4938(5)	0.2431(2)	0.63(4)
O(5) (6*i*)	0.1740(2)	−0.1740(2)	0.5929(1)	0.58(3)
	0.1739(3)	−0.1739(3)	0.5933(2)	0.40(6)
R_p = 4.40(%) 4.80		R_{wp} = 5.40(%) 5.77	χ^2 = 1.578 1.115	

[a]Site occupied by 0.5 Ga, 0.5 Zn for both compositions.
[b]Sites fully occupied by Cr for $Ba_2Sn_2ZnGa_3Cr_7O_{22}$, and by 0.86(3) Cr, 0.14(3) Ga for $Ba_2Sn_2ZnGa_4Cr_6O_{22}$.

of magnetic frustration. Full occupancy of the Kagome layers by magnetic ions has not been reported for SCGO, and the hydrothermal synthesis conditions necessary for the synthesis of jarosites make full occupancy difficult to attain in those compounds as well [2,5,11]. Thus the *QS* ferrites, although appearing to be chemically complex, are the cleanest materials presently available for study of 2D Kagomé-net based magnetic systems.

The magnetic susceptibility of the *QS* ferrites was measured between 300 and 2 K in a commercial SQUID magnetometer in an applied field of 5 T. The reciprocal susceptibility is plotted as a function of temperature in Fig. 3. The data show the classical signature of magnetic frustration: χ^{-1}(T) is linear at high temperatures, with a slope yielding a moment slightly smaller than expected for Cr^{3+} (3.73 μ_B and 3.55 μ_B per Cr^{3+} measured for the Cr_6 and Cr_7 compounds, respectively, versus an expectation of 3.87 μ_B), while a downturn is observed in χ^{-1} at lower temperatures. The ferromagnetic-like deviation from a Curie-Weiss law observed at low temperatures is common to many geometrically frustrated materials, and is distinctly different from what would be observed, for example, in a two-dimensional magnetic system undergoing short-range magnetic ordering. The large negative temperature intercepts of the high-T data are indicative of the strong antiferromagnetic pairwise interaction: $\theta_W = -315$ K for the Cr_6 compound and -312 K for Cr_7. That χ^{-1} deviates so little from the infinite-temperature limit even when the temperature is well below the mean-field energy scale $|\theta_W|$ is a hallmark of strong geometrical frustration and is related to a strong down-shift in spectral weight of magnetic excitations to lower energies. The susceptibility per chromium is lower in the Cr_7 compound than in the Cr_6 variant, providing another indication of the presence of geometrical frustration. The inset to Fig. 3 shows the magnetic susceptibility over a wide range of temperature for the Cr_6 compound and reveals a weak maximum in χ near 1.5 K, suggestive of a spin-glass transition. A similar effect was seen for the Cr_7 compound, but the magnitude of the change in χ was smaller. In both Cr_6 and Cr_7 the peak in the susceptibility is near 1.5 K. The ratio of the Weiss theta to the spin-glass transition temperature is one of the frequently employed measures of the degree of magnetic frustration [1]. In this picture, the spin-glass transition is due to the short range ordering of some fraction of the spins which are not fully locked into a frustrated state by defects or relaxations, and the spin-glass temperature is a barometer of the frustration of the overall lattice. The smaller magnetic feature in the susceptibility in Cr_7 vs Cr_6 is then due to the presence of fewer nonfrustrated spins able to participate in the spin-glass transition, as would be expected from the lower degree of disorder. Both *QS* ferrite compounds show frustration of spin freezing by the ratio $f = -\theta_W/T_{SG} \approx 200$, larger than that observed in both the spinel $ZnCr_2O_4$ or $SrCr_8Ga_4O_{19}$.

To study the low-temperature behavior of the *QS* ferrites, the specific heat $C(T)$ was measured between 0.3 and 10 K by the semiadiabatic heat pulse method for $Ba_2Sn_2ZnGa_3Cr_7O_{22}$. These data are shown in Fig. 4, where comparison is made to the specific heats of the spinel $ZnCr_2O_4$ and SCGO, $SrCr_8Ga_4O_{19}$. To consider only the contribution of the magnetism to the specific heat, the measured specific heats of the nonmagnetic analogs $ZnGa_2O_4$, $SrGa_{12}O_{19}$, and $Ba_2Sn_2ZnGa_{10}O_{22}$ have been subtracted. The temperature scale for each compound has been normalized to the effective pairwise interaction temperature θ_W. The loss of entropy at very low temperatures in $SrCr_8Ga_4O_{19}$ and $Ba_2Sn_2Ga_3ZnCr_7O_{22}$ is signaled by a broad peak in $C(T)/T$ which is unlike the sharp lambdalike feature seen upon entering a Néel state as seen in $ZnCr_2O_4$, but rather is reminiscent of

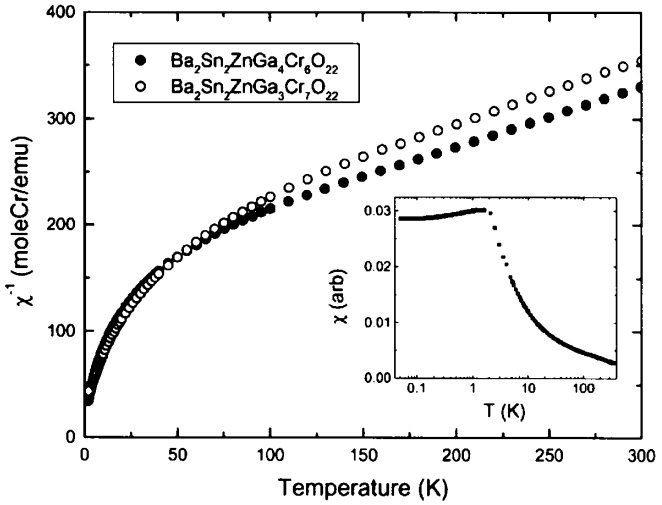

FIG. 3. Inverse magnetic susceptibility of $Ba_2Sn_2ZnGa_3Cr_7O_{22}$ and $Ba_2Sn_2ZnGa_4Cr_6O_{22}$. The inset shows the magnetic susceptibility of the Cr_6 compound on a logarithmic temperature scale.

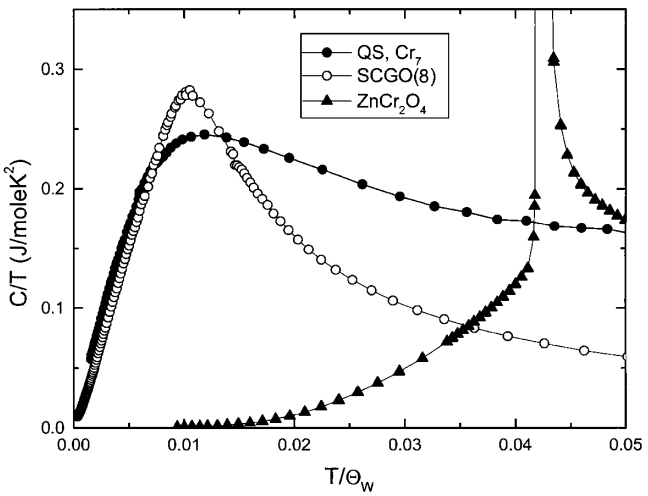

FIG. 4. Comparison of the low-temperature specific heats of $Ba_2Sn_2ZnGa_2Cr_6O_{22}$, $SrGa_4Cr_8O_{19}$, and $ZnCr_2O_4$ on a normalized temperature scale. The lattice contribution to the specific heat has been subtracted.

the short-range-order feature that typically precedes a spin-glass transition. In such cases the maximum in $C(T)/T$ occurs at temperatures roughly 50% above the spin-glass ordering temperature [1]. Below the peak, $C(T)/T$ varies linearly with T, i.e., $C(T) \sim T^2$. Normally this behavior in a two-dimensional system would signal the presence of antiferromagnetic magnons. However, the lack of an ordering anomaly in $C(T)$ argues against this explanation, since magnons are the harmonic excitations from an ordered state. The origin of this behavior is a subject of ongoing investigation but seems to be a hallmark of 2D, highly frustrated Kagomé systems. The final decrease in entropy at low temperatures represents the loss of the last of the magnetic entropy, amounting to approximately 15% of the total below $0.01\theta_W$ for both the *QS* ferrite and SCGO. Using this criterion as a measure of the shift of spin excitations to lower energy due to geometrical frustration, the *QS* ferrite and SCGO are quite below the spinel but very similar to each other. The major difference between the two layered phases is that the *QS* ferrite loses its magnetic entropy over a wider range of relative temperature above $0.01\theta_{\mathrm{CW}}$ than does SCGO.

The magnetic lattices of the three related compounds, all based on Cr^{3+}, are shown in Fig. 2. In the spinel $ZnCr_2O_4$, the magnetic Kagomé nets are fully connected in three dimensions through an additional set of magnetic sites. The strength of the pairwise spin interaction, as measured through the Curie-Weiss temperature (θ_W), is -392 K, and the three-dimensional antiferromagnetic ordering occurs at $T_N = 12$ K. Using $f = -\theta_W/T_N$ as a relative measure of magnetic frustration, the suppression of the ordering is by a factor $f = 25$. In the SCGO structure, the interlayer coupling is much weaker in the third dimension than is found in spinels: Pairs of Kagomé kagome layers are strongly coupled to each other, but only weakly coupled to adjacent pairs through intermediate magnetic sites [12]. For $SrCr_8Ga_4O_{19}$, $\theta_W = -515$ K and the magnetic ordering is of the spin-glass type ($T_{SG} = 3.5$ K), leading to an estimation of the relative frustration of $f = 150$. Finally, for the *QS* ferrite, there are no magnetic sites between spinel-like layers. The interlayer coupling is very weak, and the magnetic frustration can be estimated by $f = 200$.

These comparisons support the interpretation that reducing the interlayer coupling of Kagomé-based magnetic systems increases the frustration for attaining the magnetic ground state. For the chromium ferrites, the suppression of the magnetic ordering temperature is much more severe on initial breakup of the coupling in the third dimension on going from $ZnCr_2O_4$ to $SrCr_8Ga_4O_{19}$ than it is on breaking up the weak interlayer coupling which exists in SCGO. Comparison of the properties of *QS* ferrite and SCGO supports the conclusion [12] that the connecting magnetic sites in SCGO do not act as effectively to couple the layers as would be at first expected. The low temperature specific heats indicate that the last of the magnetic entropy is lost over a significantly more narrow range of relative temperature in the more 3D coupled SCGO than for *QS* ferrite. Decreasing the effective dimensionality is expected to suppress long-range magnetic ordering even in conventional magnetic systems, and at least part of the suppression of the ordering in the frustrated ferrites may be due to similar factors. Detailed experimental comparison to conventional perovskite based Cr^{3+} RP phases to quantify the differences in behavior on decreasing interlayer coupling would be of significant interest, as would explicit theoretical modeling of the effect of weakening 3D coupling in a system of stacked Kagomé nets. The *QS* ferrite lattice is the most structurally low dimensional of the ferrite group. Coupled with the relative ease of synthesis of materials with fully filled Kagomé nets, the *QS* ferrite phase may be the best material presently known to compare to theoretical models of Kagomé plane lattices with antiferromagnetic spin interactions.

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