

# Magnetic frustration in the spinel compounds $\text{GeCo}_2\text{O}_4$ and $\text{GeNi}_2\text{O}_4$

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In both spinel compounds  $\text{GeCo}_2\text{O}_4$  and  $\text{GeNi}_2\text{O}_4$  which order antiferromagnetically (at  $T_N=23.5$  K and  $T_N=12.13$  K/ $T_N=11.46$  K) with different Curie-Weiss temperatures ( $T_{CW}=80.5$  K and  $-15$  K), the usual magnetic frustration criterion  $f=|T_{CW}|/T_N \gg 1$  is not fulfilled. Using neutron powder diffraction and magnetization measurements up to 55 T, both compounds are found with a close magnetic ground state at low temperature and a similar magnetic behavior (but with a different energy scale), even though spin anisotropy and first neighbor exchange interactions are quite different. This magnetic behavior can be understood when considering the main four magnetic exchange interactions. Frustration mechanisms are then enlightened.

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Frustration is one of the most important problems of magnetism. First proposed by Toulouse<sup>1</sup> to explain the spin glass behavior, the concept of frustration has been generalized to systems where all the existing interactions cannot be simultaneously satisfied leading to a highly degenerated ground state. One of the main problem is to understand how this degeneracy is lifted at low temperature. Many systems have been studied<sup>2</sup> and it is clear that no general rule exists, each system “finding its own solution:” second order antisymmetric interaction (Dzialoshinsky-Moryia),<sup>3</sup> ionic anisotropy,<sup>4</sup> coupling to the lattice,<sup>5</sup> etc. Complex magnetic structures are often observed, i.e., with partially ordered magnetic sites.

There exists two types of frustration mechanisms. In the first one frustration has its origin in the geometrical arrangement of interactions as in triangular or tetrahedral lattices with first neighbor antiferromagnetic (AFM) interaction; in the second one frustration originates from competing interactions. A good example is the square lattice with ferromagnetic (FM) interactions along the sides of the square and a strong AFM interaction along the diagonals. The usual criterion for frustration is the ratio  $f=|T_{CW}|/T_N \gg 1$  between the Curie-Weiss temperature  $T_{CW}$  which is a measure of the interactions energy scale and the Néel temperature  $T_N$  below which long range order prevails. It is generally admitted that for strongly frustrated systems  $f > 10$ .

In this context, the spinel compounds  $AB_2O_4$  are objects of renewed interest: they consist of corner-sharing tetrahedra of magnetic ions  $B$  on a pyrochlore lattice (see Fig. 1) and are therefore considered as good candidates for geometrical frustration. Here we study the cases  $A=\text{Ge}$  and  $B=\text{Ni}$  or  $\text{Co}$ . According to the usual criterion,  $f > 10$ , they should not exhibit magnetic frustration. They present different spin anisotropy and first neighbor exchange interactions. In spite of this, we show that they have a close magnetic structure at low temperature and a close magnetic behavior at high field. This will be interpreted through a careful analysis of the exchange paths. Several frustration mechanisms will be enlightened that are not usually considered in these compounds. They arise both from geometry and competing interactions.

Polycrystalline samples were prepared by solid state reaction. Mixtures of  $\text{GeO}_2$  with  $\text{NiO}$  or  $\text{Co}_3\text{O}_4$  in appropriate

proportions were heated three times for 18 h at  $940^\circ\text{C}$ – $1000^\circ\text{C}$  (Co compound) or  $1140^\circ\text{C}$  (Ni compound) in air, with intermittent grinding. We checked by x-ray measurements that both compounds adopt a normal spinel structure in the  $Fd3m$  space group with  $\text{Ge}^{4+}$  ions in oxygen tetrahedral sites and magnetic ions ( $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$ ) in oxygen octahedral ones, with no inversion. The network of magnetic ions tetrahedra is regular.

The magnetic susceptibility of both compounds present a Curie-Weiss behavior at high enough temperature (300 K–800 K) (Ref. 6) indicating that  $\text{Co}^{2+}$  is in a high spin state (spin  $S=3/2$  and average gyromagnetic factor  $g=2.45$ ) and  $\text{Ni}^{2+}$  in its usual  $S=1$  state with  $g=2.34$ . The spin anisotropy is expected to be specific for each ion as well as the orbital occupancy.<sup>7</sup> In these spinels, due to the octahedral oxygen crystal field, the degeneracy of the five  $d$  or-

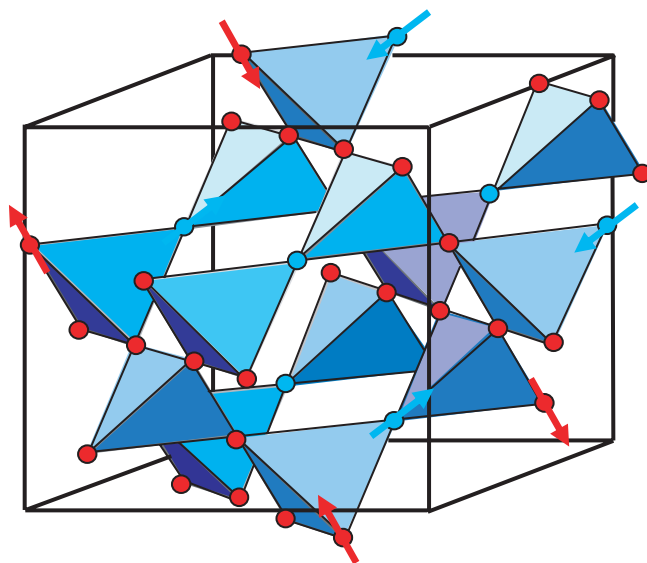


FIG. 1. (Color online) Network of magnetic ions in the cubic spinel structure showing the corner-sharing tetrahedra. Kagomé (in red) and triangular (in blue) planes are stacked along the diagonal of the cube. The AFM structure observed in  $\text{GeNi}_2\text{O}_4$  is also depicted (see text for details).

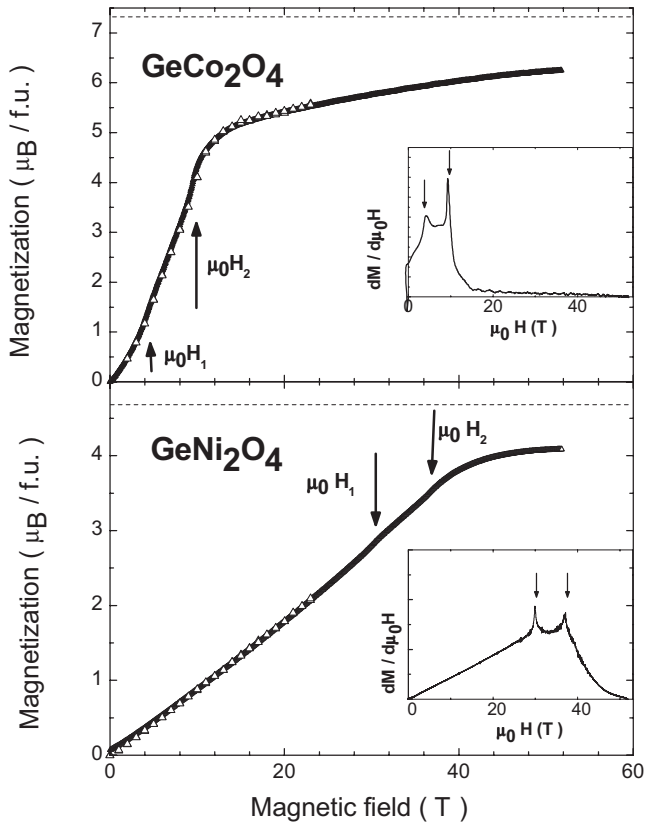


FIG. 2. Magnetization versus magnetic field in dc fields ( $\Delta$  up to 23 T) and pulsed fields ( $\blacktriangle$  up to 55 T) at 4 K, for  $\text{GeCo}_2\text{O}_4$  (a) and  $\text{GeNi}_2\text{O}_4$  (b). The dotted lines indicate the expected saturation values. Insets: derivative of the magnetization curves enhancing the two spin-flop fields. The absolute value of the magnetization was calibrated in the dc fields experiment.

bitals is lifted with three  $t_{2g}$  orbitals with smaller energy and two  $e_g$  orbitals with higher energy. The orbital occupation for the  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions differ by a hole in the  $t_{2g}$  orbitals. This changes substantially the first neighbor interaction as first indicated by their Curie-Weiss temperature: it is positive for  $\text{GeCo}_2\text{O}_4$  (+80.5 K) but smaller and negative for  $\text{GeNi}_2\text{O}_4$  (−15 K). The AFM long range order occurs at  $T_N = 23.5$  K for the Co compound and in two steps, at  $T_{N1} = 12.13$  K and  $T_{N2} = 11.46$  K, for the Ni compound, as deduced from the cusp in the susceptibility, in agreement with the literature.<sup>8–10</sup> We have performed magnetization measurements up to 23 T at the Grenoble High Magnetic Field Laboratory and in pulsed magnetic field up to 55 T at the Laboratoire National des Champs Magnétiques Pulsés. Neutron powder diffraction patterns were collected on the high resolution G4.1 and G4.2 diffractometers at the Laboratoire Léon Brillouin, in the temperature range 1.5–50 K.

The AFM long range order is characterized, for both compounds, by a strong robustness against magnetic fields: 55 T is not sufficient to align all the magnetic moments at 4 K (see Fig. 2). The most striking feature in the magnetization curves is the presence of two spin reorientation transitions at high fields ( $H_1 = 4.25$  T,  $H_2 = 9.70$  T for  $\text{GeCo}_2\text{O}_4$  and  $H_1 = 30$  T,  $H_2 = 37$  T for  $\text{GeNi}_2\text{O}_4$ ) revealing a close behavior. The field scale is higher in the Ni compound ruling out an

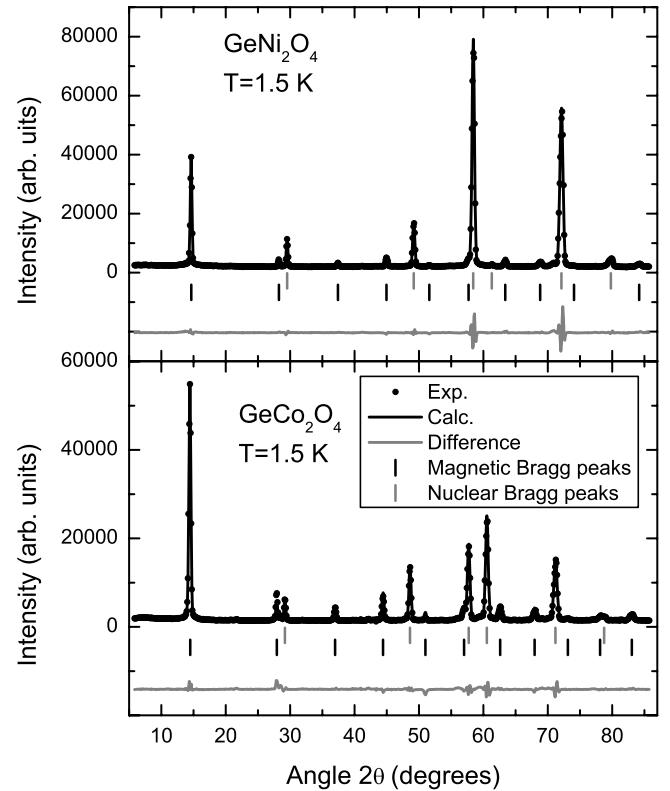


FIG. 3. Rietveld refinement of the neutron powder patterns at 1.5 K for  $\text{GeCo}_2\text{O}_4$  and  $\text{GeNi}_2\text{O}_4$  using the Fullprof package (Ref. 16) (see text).

effect of spin anisotropy (smaller for Ni) since for simple uniaxial antiferromagnets the spin-flop field is an increasing function of the anisotropy.<sup>7</sup>

The neutron diffraction measurements show also a close behavior for the Ni and Co compounds (Fig. 3). The additional Bragg peaks rising below  $T_N$ , characteristics of the AFM phase, can be indexed with the same propagation vector  $\vec{k} = (1/2, 1/2, 1/2)$ . There are four magnetic atoms in the asymmetric unit chosen on the same tetrahedron. Three of them belong to a kagomé plane and the fourth one to a triangular plane. These spin orientations are in agreement with the proposition by Bertaut *et al.*<sup>8</sup> rather than the one by Plumier.<sup>13</sup> Considering the kagomé and triangular planes stacked along the (111) direction (Fig. 1), all the spins in one given plane are parallel to each other and antiparallel from one kagomé (or triangular) plane to another. The kagomé site moments are in the plane perpendicular to the (111) direction. For the triangular site moments, two different orientations of the moments, parallel or perpendicular to the (111) direction, yield close solutions. The diffraction pattern is slightly better fitted with the moments parallel ( $\text{GeNi}_2\text{O}_4$ ) or perpendicular ( $\text{GeCo}_2\text{O}_4$ ) to the (111) direction. The exact orientation in this plane cannot be determined from powder diffraction. The refined moments are reported in Table I. For  $\text{GeCo}_2\text{O}_4$ , the amplitude of the magnetic moments is found identical for the four magnetic sites but is substantially smaller than the value deduced from the high temperature susceptibility and high field magnetization:  $3.01\mu_B$  instead of  $3.67\mu_B$ . For  $\text{GeNi}_2\text{O}_4$ , it is quite close for the kagomé site

TABLE I. Amplitude of the magnetic moments, in  $\text{GeNi}_2\text{O}_4$  and  $\text{GeCo}_2\text{O}_4$  with lattice parameter  $a=8.340$  Å and  $8.251$  Å, respectively, determined from Rietveld refinement of the neutron diffraction powder patterns at 1.5 K.

$\text{GeCo}_2\text{O}_4$	$x$	$y$	$z$	$\mu(\mu_B)$
$\text{Co}_1$	0.00	0.25	0.75	3.02(1)
$\text{Co}_2$	0.25	0.25	0.50	3.02(1)
$\text{Co}_3$	0.25	0.00	0.75	3.02(1)
$\text{Co}_4$	0.00	0.00	0.50	3.02(1)

Nuclear phase: Bragg  $R$  factor=2.05, Rf factor=1.07

Magnetic phase:  $R$  factor=5.91

$\text{GeNi}_2\text{O}_4$	$x$	$y$	$z$	$\mu(\mu_B)$
$\text{Ni}_1$	0.00	0.25	0.75	2.29(2)
$\text{Ni}_2$	0.25	0.25	0.50	2.29(2)
$\text{Ni}_3$	0.25	0.00	0.75	2.29(2)
$\text{Ni}_4$	0.00	0.00	0.50	1.10(20)

Nuclear phase: Bragg  $R$  factor=2.59, Rf factor=1.78

Magnetic phase:  $R$  factor=8.33

moments:  $2.29\mu_B$  instead of  $2.35\mu_B$  but reduced for the triangular site moment,  $1.10\mu_B$ . These reduced magnetic moments are reminiscent of what is observed in the other compound with the same magnetic network  $\text{GdTi}_2\text{O}_7$ , where one spin out of four on average is not ordered.<sup>11</sup> There, the magnetic structure is described by the same propagation vector but the alignment of the spins in one given plane adopts the  $120^\circ$  structure typical of triangle-based networks of frustrated antiferromagnets.<sup>12</sup> Note that the presence of two decoupled AFM sets of FM sublattices observed in the Co and Ni spinels is in agreement with the presence of two reorientation fields in the magnetization process, one corresponding to each set of sublattices.

The great variety of magnetic ground states observed in pyrochlores and spinels arises from strong magnetic frustration mechanisms. The degeneracy of the magnetic ground state is lifted by additional mechanisms that may differ substantially from one compound to the other. A good knowledge of the magnetic interactions involved in these systems is crucial for the understanding of their magnetic properties. It implies identifying and sorting out the different relevant magnetic exchange paths within the magnetic network and via the oxygen network. All these interactions depend on the magnetic and oxygen ions orbitals through their particular occupancy and spatial distribution. We have carefully examined the case of  $\text{GeCo}_2\text{O}_4$  and  $\text{GeNi}_2\text{O}_4$  (Figs. 4 and 5) using Goodenough-Anderson-Kanamori rules.<sup>14</sup> The dominant interactions between the magnetic  $B$  ions to be considered are those from the direct exchange, the  $90^\circ$  super exchange, and the  $135^\circ$  and  $180^\circ$  super super exchange. The direct  $B$ - $B$  interaction is strong and FM for  $\text{Co}^{2+}$  and null for  $\text{Ni}^{2+}$ , respectively, due to the presence or not of a hole in the  $t_{2g}$  orbital. The  $90^\circ$   $B$ - $O$ - $B$  super exchange is FM and weak. Both of them will be described by the effective first neighbor interaction  $J_1$ . There are two different super-super exchange paths  $B$ - $O$ - $O$ - $B$  at  $135^\circ$  for the third neighbors interaction

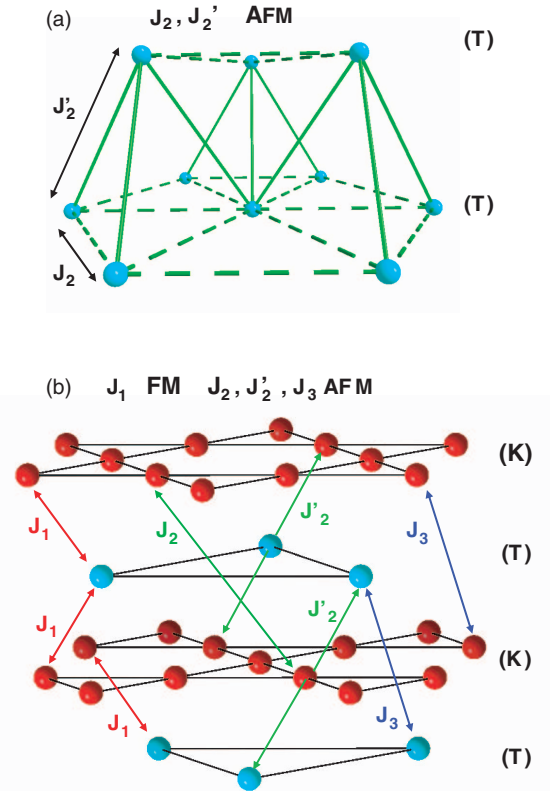


FIG. 4. (Color online) Magnetic ions in the kagomé ( $K$ ) and triangular planes ( $T$ ). (a) Geometric frustration in the  $J_2/J_2'$  network when only the triangular planes are considered. The (non)satisfied ( $J_2$ )  $J_2'$  are depicted by (dis)continuous lines. (b) Competition between  $J_1$  (whatever its sign) and AFM  $J_2$ ,  $J_2'$ , and  $J_3$ .

yielding AFM  $J_2'$  and  $J_2$ , with and without an interstitial magnetic ion, respectively. They therefore differ, in the Co compound only, from an additional small FM direct exchange contribution. Finally, there is the AFM  $180^\circ$   $B$ - $O$ - $O$ - $B$   $J_3$  interaction between the sixth neighbors, whose contribution was also considered in Ref. 8. The other exchange paths yield negligible contributions. Note that the above analysis rules out any geometrical frustration mechanisms within the nearest-neighbor tetrahedra since  $J_1$  is FM, which is in sharp contrast to the Gd (Ref. 11) or Cr compounds.<sup>5</sup>

In order to test whether these exchange path considerations alone may account for the observed magnetic structures, we have performed a zero temperature analysis of the wave vectors of possible instabilities for a Heisenberg model  $H = -\sum_{ij} J_{ij} S_i \cdot S_j$  within the  $(J_2/J_1, J_2'/J_1, J_3/J_1)$  phase space.<sup>15</sup> We found that, for  $-2 < J_i/J_1 < +2$ , there are two finite regions of parameters for which the instability wave vector belongs to the  $q$ -star  $(1/2, 1/2, 1/2)$ , as observed experimentally, with a corresponding nondegenerate eigenmode in reciprocal space  $(1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3}, 0)$  and its cyclic permutations. Within this approach, the ground state is described by FM kagomé planes, as observed experimentally, and nonmagnetic triangular planes. This latter feature, with one disordered site over four in average, seems to apply partially to the Ni compound where a reduced moment is observed for the fourth spin. Clearly, an additional mechanism

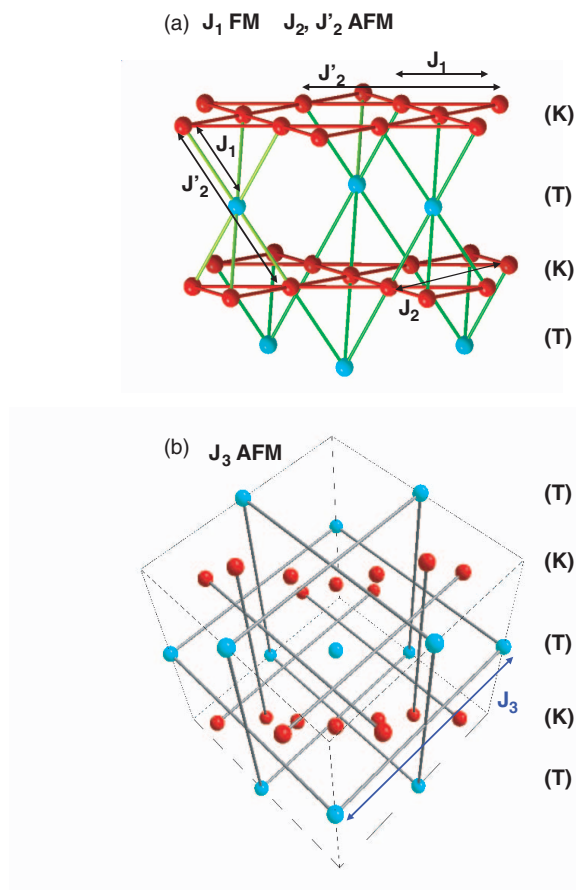


FIG. 5. (Color online) (a) Competing FM  $J_1$  and AFM  $J_2'$  interactions. In the (K) planes,  $J_1$  dominates, in between the (K) planes,  $J_2'$  dominates. The AFM  $J_2$  interaction is also depicted. (b) Network of the AFM  $J_3$  interactions.

operates to select a particular orientation for this spin, which differs in the Co and Ni spinels. This is revealed in the orientation of the ordered part of the fourth spin [perpendicular

or parallel to (111), respectively, in both compounds]; it may also be related to the two main spin-reorientation processes in the magnetization curve which occur at different fields and magnetization values.

In the light of the above analysis, it appears that several frustration mechanisms are present. For instance, the network formed by the AFM  $J_2'$  and  $J_2$  interactions within and in between the triangular planes consists of tetrahedra connected by their edges where geometrical frustration takes place [Fig. 4(a)]. Even more striking is the competition between  $J_1$  on one side (whatever its sign) which couples a kagomé plane with a triangular plane and vice versa, and the AFM interactions  $J_2$ ,  $J_2'$ , and  $J_3$  on the other side, which couple identical planes (either kagomé or triangular) [Fig. 4(b)]. These two frustration mechanisms are relevant for any B site magnetic spinel. For  $B=(\text{Ni},\text{Co})$ , there is additionally a competition between the FM  $J_1$  and the AFM  $J_2$  [Fig. 5(a)]. Finally, the only magnetic interaction which is always satisfied within the observed magnetic structure is the  $180^\circ$  super-super exchange interaction  $J_3$  [Fig. 5(b)].

In conclusion, we have shown that  $\text{GeCo}_2\text{O}_4$  and  $\text{GeNi}_2\text{O}_4$  present an original magnetic ground state, with a  $(1/2, 1/2, 1/2)$  propagation vector and four magnetic sublattices (AFM stacking of FM kagomé planes intercalated with AFM stacking of FM triangular planes). Due to the presence of these sublattices, the field induced common magnetic behavior of both compounds present two spin reorientation transitions in high fields. Frustration mechanisms take place in these systems although not as straightforward as in other spinels and pyrochlores with AFM first neighbor interactions. This study underlines the need to consider exchange paths for the magnetic interactions that are well beyond first neighbors in systems dominated by magnetic frustration.

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