Strong magnetic fluctuations in transition metal oxides (invited)

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Most magnets have long-range magnetic order when the thermal energy is less than the local magnetic exchange energy \( (T<\Theta_{cw}) \). Effects such as reduced dimensionality and frustration, however, can suppress the ordering transition and lead to unusual cooperative paramagnetic phases at low temperatures. We review neutron scattering experiments exploring such short-range-ordered phases in insulating transition metal oxides. We discuss \((V_{1-x}Cr_x)O_3\), in which orbital fluctuations appear to limit spin correlations to within small "molecular" clusters, \(SrCrO_3\), \(Ga_{12-9p}O_{19}\), in which geometrical frustration allows local antiferromagnetic constraints to be fulfilled without long-ranged order, and \(Y_2BaNiO_5\), in which magnetic interactions occur only within chains of spins which are unable to order because of the Haldane effect. Emphasis is placed on the common features of exchange interactions in these oxides and the important role which magnetic neutron scattering has played in understanding the unusual magnetic phenomena. © 1996 American Institute of Physics.

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I. INTRODUCTION

A common structural unit in magnetism is a transition series cation surrounded by six oxygen ions at the vertices of an octahedron.\(^1\) This unit, for example, is the source of interacting magnetic moments in classical three-dimensional antiferromagnets such as \(MnO\), \(FeO\), \(CoO\), \(NiO\), \(Fe_2O_3\), and \(Cr_2O_3\). Adjoining octahedra, however, can also build periodic structures whose connectivity is not conducive to the development of conventional long-ranged order, and therefore may give rise to novel cooperative magnetic phenomena. In this article we review experiments examining such magnetic oxides which have strong magnetic fluctuations and short-ranged spin correlations even at low temperatures \((T<\Theta_{cw})\).

The neutron scattering techniques pioneered by Shull and Brockhouse are irreplaceable tools for elucidating spin correlations in these systems, much as they were for conventional Neel antiferromagnets.\(^2\) The measured quantity is the probability that a neutron with a wave vector \(k_i\) is scattered into a final state with wave vector \(k_f\) through its interaction with the sample. Under suitable conditions this scattering process may be treated in the Born approximation, and in this case the scattering probability distribution is proportional to the neutron scattering cross section, which depends only on wave vector transfer, \(Q=k_f-k_i\), and energy transfer, \(h\omega=(\hbar^2/2m)(k_f^2-k_i^2)\). Here we consider only the magnetic part of the scattering cross section, which is proportional to

\[
I_m(Q,\omega) = \sum_{\alpha \beta} \langle \hat{Q}_\alpha \hat{Q}_\beta \rangle S^{\alpha\beta}(Q,\omega),
\]

where \(S^{\alpha\beta}(Q,\omega)\) is the dynamical spin correlation function,

\[
S^{\alpha\beta}(Q,\omega) = |F(Q)|^2 \frac{(g\mu_B)^2}{2\pi\hbar} \int dt e^{i\omega t} \times \frac{1}{N} \sum_{RR'} \langle S^\alpha_R(t) S^\beta_{R'}(0) \rangle e^{-i(Q \cdot (R'-R))},
\]

which contains unique information about magnetic correlations in the sample. In this expression \(F(Q)\) is the magnetic form factor, a property of the 3d orbitals.\(^3\)

For powder samples the information available from magnetic neutron scattering is less specific than for single crystals, because the scattered intensity only depends on \(Q=|k_f-k_i|\) and is proportional to the spherically averaged dynamic spin correlation function

\[
\langle S(Q,\omega) \rangle = \int \frac{dQ}{4\pi} \frac{1}{2} I_m(Q,\omega).
\]

Nonetheless, as we shall see, important results may still be extracted, especially in the small \(Q\) limit or when we are interested in Brillouin zone averaged quantities.

For comparison with bulk measurements, and between different neutron scattering experiments, we have in most cases measured scattering cross sections in absolute units. The scale factor between the detector count rate and the quantities of Eqs. (1)–(3) were determined by normalizing to count rates associated with known nuclear scattering cross sections of the samples.

II. ORBITAL FLUCTUATIONS IN \(V_{1-x}Cr_xO_3\)?

\(V_2O_3\) can be insulating or metallic and antiferromagnetic or paramagnetic depending on temperature, pressure, and exact stoichiometry,\(^4\) and consequently the material has been a testing ground for theories of electronic correlations and
antiferromagnetic structure which is unique for corundum transition which takes place at though these interactions would appear to yield a three-atom system. This has two important consequences: (1) \( V_2O_3 \) has only two \( 3d \) electrons which occupy the crystal field triplet \( t_2g \). The \( t_2g \) orbitals have significant overlap only with their counterparts on neighboring vanadium atoms and this has two important consequences: (1) \( V_2O_3 \) is a Mott insulator as opposed to a charge transfer insulator. (2) Direct cation–cation overlap between in-plane nearest neighbors and the one out-of-plane nearest neighbor are the dominant sources of magnetic exchange interactions. Even though these interactions would appear to yield a three-dimensional nonfrustrated antiferromagnet, the magnetic transition which takes place at \( T_N=180 \) K is unusual because (1) it occurs far below \( T_N=350 \) K, (2) it involves an antiferromagnetic structure which is unique for corundum transition metal oxides, (3) it is accompanied by a lattice distortion, and (4) it is a first order transition.

To explore this unusual magnetic phase transition, we have examined spin correlations in the paramagnetic phase by inelastic magnetic neutron scattering. Figure 2 shows the wave vector dependence of neutron scattering at \( T=205 \) K and \( h\omega=3 \) meV. For \( Q \) along the (101) direction we find two well-defined peaks which, in being almost as wide as the projection of the first Brillouin zone in that direction, imply that magnetic correlations involve only nearest neighbors. The data are qualitatively different from those derived from paramagnetic scattering in conventional three-dimensional antiferromagnets, not only because the correlations are so short ranged for \( T/T_N=1=0.08 \), but also because coherent scattering dominates over incoherent scattering despite the very short correlation lengths. Correlations are so short ranged, in fact, that we can fit the data to a truncated lattice sum which neglects all but the correlations between nearest neighbors,

\[
S(Q) = \sum_{R,R'} \langle S_R S_{R'} \rangle \exp(iQ\cdot(R-R')).
\]

The best fit, which also describes \((h,0,-5)\) and \((h01)\) scans at \( h\omega=3 \) meV, is shown as a solid line in Fig. 2. From the fit we obtain values for nearest-neighbor spin correlations: \( \langle S_{(0,0,0)} S_{(0,0,0)} \rangle = 0.6(3) \), \( \langle S_{(0,0,0)} S_{(1/2,2/3,0)} \rangle = -0.19(8) \), \( \langle S_{(0,0,0)} S_{(1/2,2/3,1/6)} \rangle = -0.18(8) \), and \( \langle S_{(0,0,0)} S_{(1/2,3/2,1/6)} \rangle = -0.09(3) \) where \( \delta = 0.026 \). These values were normalized so that \( \langle S_{(0,0,0)} S_{(0,0,0)} \rangle = 1 \). Figure 3 shows that it is not a lack of interactions that prevents longer-ranged correlations from developing. The full widths at half-maximum (FWHM) of constant-\( h\omega \) scans along the (101) direction through the peak at \( Q=(101) \) are almost indistinguishable from those at \( h\omega=3 \) meV, for energy transfers, \( h\omega \), as high as 18 meV. Also the nearly \( h\omega \)-independent peak amplitudes indicate that these correlations may persist to even higher energies.

The \( Q \) dependence of paramagnetic scattering from \((V_{1.97}Cr_{0.03})O_3\) resembles that of energy integrated scattering from isolated spin clusters in dilute magnets. However, the energy spectrum is continuous indicating that we are dealing with excitations in a macroscopic physical system. A possible explanation for this unusual behavior was recently proposed by Rice. His idea is that orbital fluctuations in the paramagnetic phase of \((V_{1-Cr})O_3\) inhibit long-ranged spin correlations through their effect on exchange interactions. In his description, which is based on the work of Castellan et al., one \( d \) electron is occupied in covalent bonding with the out-of-plane nearest neighbor while the other must choose which of the three in-plane vanadium neighbors to bond with. Pairs which bond have ferromagnetic spin–spin interactions which connect them into doubly occupied clusters.\(^{11}\)
interaction whereas those which do not interact antiferromagnetically, and this leads to an effective spin–orbit coupling which cannot be accounted for by a conventional spin Hamiltonian. In this theory the coupling of the spin system to orbital fluctuations is what inhibits the development of spin order for \( T' \) and the magnetic transition is actually driven by an orbital ordering transition. In particular, the orbital order enables the development of long-ranged spin order by establishing an ordered array of spin exchange interactions. Further neutron scattering experiments probing the effects of orbital fluctuations on spin fluctuations both in the low and high temperature phases are underway to test this hypothesis.

III. ISOLATED SPIN PAIRS AND FRUSTRATION IN \( \text{SrCr}_{9p}\text{Ga}_{12-9p}\text{O}_{19} \)

\( \text{SrCr}_{9p}\text{Ga}_{12-9p}\text{O}_{19} \) is a more complicated substance than most condensed matter physicists are normally willing to consider. Nonetheless, the unique magnetic properties of this insulating oxide do warrant attention. The bulk properties which called our attention to \( \text{SrCr}_{9p}\text{Ga}_{12-9p}\text{O}_{19} \) were (1) a magnetic susceptibility which follows Curie–Weiss behavior with \( \Theta_{\text{CW}}=-500 \) K down to \( T \approx 100 \) K, (2) the absence of static order until a spin-glass-like transition at \( T_g=3.5 \) K \( \leq |\Theta_{\text{CW}}| \), and (3) low temperature specific heat data, \( C(T) \), which in being proportional to \( T^2 \) resembles a long-range ordered two-dimensional magnet more than a conventional spin glass for which \( C \sim T^\beta \).

The aspects of the crystal structure which are relevant for this discussion are shown in Fig. 4. As in \( \text{V}_2\text{O}_3 \), the trivalent magnetic cation, in this case \( \text{Cr}^{3+} \), is surrounded by a distorted octahedron of oxygen atoms. The cation lattice is however more complicated in this case, encompassing three distinct sites which are denoted \( 12k \), \( 2a \), and \( 4f_{via} \). The \( 12k \) layer is a slightly distorted Kagomé lattice whereas the \( 2a \) and \( 4f_{via} \) layers are triangular lattices. The \( \text{Cr}^{3+} \) ions in the \( 12k-2a-12k \) block form corner-sharing tetrahedra, as in three-layer (111) slabs of the trivalent cation sites in the cubic pyrochlore \( \text{Cr}_2\text{O}_2\text{Fe}_2\text{O}_4 \) and spinel structures.

Neutron scattering experiments have enabled us to derive a comprehensive model of magnetic interactions in this material, and to identify the three-layer \( 12k-2a-12k \) slab as the origin of the two-dimensional frustrated magnetism in \( \text{SrCr}_{9p}\text{Ga}_{12-9p}\text{O}_{19} \). Figure 5 shows wave vector integrated inelastic neutron scattering, \( S(\omega) \), at \( T=1.3 \) K from a powder sample of \( \text{SrCr}_{9p}\text{Ga}_{12-9p}\text{O}_{19} \) with \( p=0.92(5) \). Apart from the usual features, the data show a very pronounced feature at \( \omega=1139 \) meV which is similar to the feature at \( \omega=1200 \) meV seen in \( \text{SrCu}_{8.8}\text{Ag}_{0.2}\text{O}_{19} \) and \( \text{SrCu}_{9.8}\text{Ag}_{0.2}\text{O}_{19} \).
from the incoherent elastic peak and a broad spectrum of magnetic scattering visible from 0 to 40 meV, we notice a resolution limited peak at $h\omega=18.6$ meV. Because the peak is sharp in wave-vector-integrated data, it must be associated with a nondispersive excitation and is therefore likely to arise from single atoms, or small clusters of atoms, which are decoupled from the rest of the system. From the $Q$ dependence of the energy-integrated intensity of the ridge, shown in Fig. 6, we can conclude that it arises from (i) a local vibrational excitation, because the intensity decreases with $Q$ and (ii) a crystal field excitation on a single chromium atom, because the $Q$ dependence is distinguishable from the magnetic form factor for chromium.\textsuperscript{17} Instead, the $Q$ dependence of the scattering closely resembles that from an isolated pair of antiferromagnetically interacting spins,\textsuperscript{9} shown as a solid line in Fig. 6. Such spin pairs also provide a detailed account for the energy and temperature dependence of the data, including a peak in $S(\omega)$ at $h\omega=37.2$ meV which only appears for $T>100$ K.\textsuperscript{16}

Considering also the values of the two fitting parameters which went into calculating the solid line in Fig. 6 and the position of the peak in Fig. 5, we conclude that there are $0.7(1)$ isolated spin pairs per formula unit in SrCr$_9$Ga$_{12-9p}$O$_{19}$ [$p=0.92(5)$]. Spins of a pair are separated by $R=2.68(7)$ Å and interact antiferromagnetically with an exchange coupling constant $J=18.6(1)$ meV. Since $4f_{vi}$ spins are the only spins which each are part of a unique spin pair, and since there are $0.78 4f_{vi}$ spin pairs per formula unit separated by $2.681(3)$ Å in our sample, it is likely that the $4f_{vi}$ Cr$^{3+}$ ions are the ones forming isolated spin pairs in SrCr$_9$Ga$_{12-9p}$O$_{19}$.

The oxygen octahedra of chromium ions in adjacent $4f_{vi}$ planes share a common face whereas the oxygen octahedra of neighboring $4f_{vi}$ and $12k$ sites share a corner. The exact same environment exists in corundum Cr$_2$O$_3$ where it has been established\textsuperscript{18} that the exchange constant between Cr$^{3+}$ ions with corner sharing oxygen octahedra is only 0.2 meV because occupied $3d$ orbitals in Cr$^{3+}$ do not overlap oxygen orbitals.\textsuperscript{1} Occupied orbitals of Cr$^{3+}$ ions in face sharing octahedra, however, have appreciable direct overlap which in Cr$_2$O$_3$ gives rise to a 15 meV antiferromagnetic exchange coupling. This number, being close to the 18.6 meV exchange constant for spin pairs in SCGO [$p=0.92(5)$], supports our comparison to Cr$_2$O$_3$ and our conclusion that $4f_{vi}$ spin pairs form isolated singlets in SrCr$_9$Ga$_{12-9p}$O$_{19}$.

Having accounted for the $4f_{vi}$ chromium sites we are left with the quasi-two-dimensional magnet consisting of a triangular lattice ($2a$) sandwiched between two Kagomé lattices ($12k$). Alternatively this lattice can be described as a three-layer (111) slab of the trivalent cation sites in the cubic pyrochlore or spinel structures. The oxygen octahedra of nearest neighbors within this spin system all share an edge and exchange interactions are therefore expected to be comparable in magnitude. Fitting high temperature bulk susceptibility data to the sum of the susceptibility of the $4f_{vi}$ and $37.2$ meV which only appears for $T>100$ K.\textsuperscript{16} Evidently it is the reduced dimensionality and unique connectivity within this three-layer magnetic which give rise to the unusual cooperative magnetic properties of SrCr$_9$Ga$_{12-9p}$O$_{19}$. We have performed a number of neutron scattering experiments to explore these properties.\textsuperscript{19} Our most interesting data are perhaps those establishing the $Q$ dependence of elastic magnetic scattering in the spin glass phase.\textsuperscript{20} The data, shown in Fig. 7, were obtained by subtracting elastic scattering at $T=70$ K from the same at $T=70$ mK. Since the half-width at half-maximum (HWHM) of the energy resolution function in this experiment was 7.5 $\mu$eV (circles) and 2.25 $\mu$eV (squares) this measurement probes magnetic correlations which persist on the nanosecond time scale. From the wave vector integral of the data we
conclude that the frozen moment in this system is only \( 1.9(2) \mu_B \), which is less than half of the frozen moment in a conventional Neél state formed by \( S = 3/2 \) \( \text{Cr}^{3+} \) ions and thus implies that quantum spin fluctuations are strong in this insulating magnet. The elastic magnetic scattering is also unusual in that although we are dealing with a concentrated magnet with only weak structural disorder, there are no sharp peaks in the data, implying that long-ranged magnetic correlations are absent. Instead the broad peak at wave vector \( Q = 1.5 \AA^{-1} \) indicates the presence of short-range antiferromagnetic correlations. Since the width of the peak is comparable to its displacement from \( Q = 0 \), static magnetic correlations are only maintained between nearest neighbors. Nonetheless, \( S(Q) \) appears to vanish as \( Q \to 0 \). A vanishing forward cross section is very significant, because it implies that there exists a decomposition of the frozen spin state into subgroups of spins which possess net spin zero. The zero spin subgroups could be pairs, triangles, or tetrahedra of nearest-neighbor \( \text{Cr}^{3+} \) ions. Although such a spin configuration in principle could be concocted on most lattices, it appears to be the unique connectivity of the pyrochlore slab which makes such a spin configuration energetically favorable by allowing for all antiferromagnetic interactions to be satisfied without establishing long-ranged order. In this respect the frozen spin configuration in \( \text{SrCr}_9 \text{Ga}_{12-2p} \text{O}_{19} \) resembles the ground state of the weakly diluted classical Kagomé antiferromagnet which Shender et al.\(^{21} \) have found to obey a “rule of satisfied triangles.”

IV. HALDANE GAP AND HOLE DOPING IN \( Y_2\text{BaNiO}_5 \)

The combination of low dimensionality and a low integer spin quantum number \((S=1)\) causes \( Y_2\text{BaNiO}_5 \) to be a rare example of a transition metal oxide which evades magnetic order down to temperatures as low as 50 mK.\(^{22} \) One dimensionality in this material comes about because oxygen octahedra, which coordinate \( \text{Ni}^{2+} \), share a corner only for \( \text{Ni}^{2+} \) ions displaced along the \( a \) axis. Because \( \text{Ni}^{2+} (3d^8) \) has more than three \( 3d \) electrons, the superexchange interactions between such magnetic cations are strong,\(^1 \) and by dominating over all other exchange interactions, yield a one-dimensional antiferromagnet (see Fig. 8).

The consequences of this microscopic solid state chemistry for the magnetic properties of the material are quite astonishing. Figure 9, for example, shows the \( Q \) dependence of inelastic neutron scattering from a powder sample for \( T=10 \, \text{K} \) and \( h\omega = 6 \, \text{meV} \) (open circles) and \( h\omega = 9 \, \text{meV} \) (filled circles). Background was measured for each of these scans at \( h\omega = -6 \) and \(-9 \, \text{meV} \), respectively, and subtracted. The horizontal bar corresponds to the FWHM \( Q \) resolution. The experiment was performed on the thermal neutron triple axis spectrometer BT2 at NIST with \( E_i = 40.3 \, \text{meV} \) and collimations \( 60^\circ - 20^\circ - 42^\circ - 44^\circ \) around the PG(002) monochromator and analyzer. A 2-in.-thick PG filter preceded the monochromator. (Adapted from Ref. 32.)

\[ \text{FIG. 8. Structure of } Y_2\text{BaNiO}_5. \text{ The oxygen ion which is a member of the octahedral coordination of two nickel ions mediates superexchange along the spin chain. (From Ref. 31.) Holes reside on this atom for } Y_{1.90}\text{Ca}_{0.10}\text{BaNiO}_5. \]

\[ \text{FIG. 9. } Q \text{ dependence of inelastic magnetic scattering from a powder sample of } Y_2\text{BaNiO}_5 \text{ at } T=10 \, \text{K} \text{ for } h\omega = 6 \, \text{meV} \text{ (open circles) and } h\omega = 9 \, \text{meV} \text{ (filled circles). Background was measured for each of these scans at } h\omega = -6 \text{ and } -9 \, \text{meV} \text{, respectively, and subtracted. The horizontal bar corresponds to the FWHM } Q \text{ resolution. The experiment was performed on the thermal neutron triple axis spectrometer BT2 at NIST with } E_i = 40.3 \, \text{meV} \text{ and collimations } 60^\circ - 20^\circ - 42^\circ - 44^\circ \text{ around the PG(002) monochromator and analyzer. A 2-in.-thick PG filter preceded the monochromator. (Adapted from Ref. 32.)} \]
placed on the superexchange mediating oxygen atoms of the (NiO$_2$)$_8$ chains by substituting Ca$^{2+}$ for Y$^{3+}$. This leads to a simple yet novel many-body system: Charge carriers interacting with a quantum spin liquid. The open triangles in Fig. 10 show that hole doping both introduces a subgap resonance peculiar to hole-doped samples. The simplest model which may be relevant for understanding the subgap resonance treats holes as static perturbations in the superexchange. In the analogous phonon problem a localized perturbation of interactions leads to a bound state or localized “optical” mode. A recent theoretical analysis of such a model has indeed identified a subgap resonance pinned to the middle of the Haldane gap when the impurity bond strength modulation exceeds a certain threshold.\textsuperscript{30}

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