The observation of magnetic excitations in a single layered and a bilayered brownmillerite

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Abstract

We describe the results of an inelastic neutron scattering measurement of the magnetic excitations in $SrCaGaMnO_{5+\delta}$, a quasi-two-dimensional compound whose structure consists of layers of MnO_6 octahedra separated by layers of GaO_4 tetrahedra (the brownmillerite structure), and $Ca_{2.5}Sr_{0.5}Mn_2GaO_8$, a bilayered brownmillerite. In both materials, a band of magnetic scattering appears below the magnetic ordering temperature which can be associated with magnon excitations. Our measurements allow us to provide an estimate for the intraplane exchange constant in both materials, which we find to be 3.4(4) meV for $SrCaGaMnO_{5+\delta}$ and 2.2(4) meV for $Ca_{2.5}Sr_{0.5}Mn_2GaO_8$.

(Some figures in this article are in colour only in the electronic version)

The production of high-purity powder samples of novel manganate structures allows the exploration of the intricate balance between the charge, orbital and spin degrees of freedom which gives rise to the complex phase diagrams typical in these highly correlated systems. Though much research on naturally layered manganates has focused on the Ruddlesden–Popper (RP) series $A_{n+1}Mn_nO_{3n+1}$ [1], some of which exhibit colossal magnetoresistance [2, 3], an alternative strategy is to consider the family of anion-deficient perovskites which adopt the brownmillerite structure[5]. In the RP phases, n layers of MnO_6 octahedra are separated by rock salt layers. For the brownmillerites considered in this paper, the separation is provided by layers of GaO_4 tetrahedra, and the resulting general formula is therefore $A_{n+1}Mn_nGaO_{3n+2}$.

[5] The structure is named after the chemist L T Brownmiller.

In this paper we present results on two, well-characterized brownmillerite compounds. The first has formula $SrCaGaMnO_{5+\delta}$ [4][6] and adopts the $n = 1$ brownmillerite structure. It is thus a quasi-two-dimensional compound consisting of single layers of MnO_6 octahedra separated by single layers of GaO_4 tetrahedra [4]. In this system the ability of the electrons to travel perpendicular to the MnO_6 layers is impaired due to the filled electron orbitals of the $Ga(d^{10})$ ions present so that superexchange interactions are heavily suppressed perpendicular to the octahedral layers. Nevertheless the system exhibits 3D G-type antiferromagnetic order. The critical temperature is 178.9(2) K [4] and there is a net canting of moments that increases on cooling, leading to increasing magnetization as the temperature approaches zero. This has been measured down to 2 K and there is no sign of a cusp indicating a low-temperature phase transition. The second material has formula $Ca_{2.5}Sr_{0.5}Mn_2GaO_8$, and has a bilayered ($n = 2$) brownmillerite structure [5, 6]. It has a transition to long-range magnetic order at 125 K. At this point the resistivity decreases by an order of magnitude and large magnetoresistance is measured ($\sim$50% at 8 T and 110 K [5]). This composition was chosen because the products of initial attempts to synthesize the composition $Ca_3GaMn_2O_8$ contained small quantities ($\sim$5%) of $CaMnO_{3-\delta}$, which develops [7] a readily detected spontaneous magnetization on cooling below 125 K. In an effort to eliminate the impurity we prepared compounds with formula $Ca_{3-x}Sr_xGaMn_2O_8$ ($0 < x < 0.6$) and established, on the basis of magnetization data, that the $CaMnO_{3-\delta}$ content is minimized in $Ca_{2.5}Sr_{0.5}Mn_2GaO_8$ [5].

There have been a number of studies of the physical properties of these brownmillerite systems using various experimental techniques, but little is known about the magnetic excitations. We have therefore performed an inelastic neutron scattering (INS) study of powder samples of both materials in order to search for magnon modes. The samples were prepared as described elsewhere [4, 5]. Each sample was packed into a cylindrical aluminium can of diameter 49 mm and thickness 1 mm and placed with the cylindrical axis at 45° to a beam of neutrons with incident energy 67 meV (wavelength 1.1 Å) in the time-of-flight (TOF) spectrometer IN4 at the ILL. The TOF technique allows a single measurement to capture data with a range of energy and wavevector transfers. The estimated resolution is 3.7 meV FWHM at the elastic line, and is expected to be similar at higher energy transfers. The measured time dependences of neutron counts scattered at various angles were combined to produce the scattering function as a function of energy and wavevector transfer. Data were recorded at three temperatures, 1.5, 50 and 200 K, so that the two lower temperatures were below the magnetic transition in each sample.

The INS data for the two samples are shown in figures 1(a)–(f). As the samples are powders, the measured dispersion is an angular average of scattering from different directions of the scattered wavevector. At the bottom of each figure, some quasielastic scattering is visible associated with Bragg peaks (the scattering for energy transfers below 5 meV is not plotted in order to bring out the higher energy inelastic features of the data). There is also a broad band of scattering at energies below 30–40 meV that increases with wavevector transfer Q and which is associated with scattering from phonons. However, most interestingly, there is a localized region of low-Q scattering centred around 25 meV for $SrCaMnGaO_{5+\delta}$ which is particularly prominent in the 1.5 K data (figure 1(a)), but is somewhat broader and weaker at 50 K (figure 1(b)), and disappears completely by 200 K (figure 1(c)). There is a much broader band of low-Q scattering observed in $Ca_{2.5}Sr_{0.5}Mn_2GaO_8$ in the energy range 10–20 meV which is also most prominent in the 1.5 K data (figure 1(d)), broader and weaker at 50 K (figure 1(e)), and disappears completely by 200 K (figure 1(f)). In both compounds, the feature disappears above $Q \sim 3$ Å^{-1}, which is consistent with the behaviour of the Mn

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[6] It is not always possible to prepare this compound in a fully reduced form; for our sample $\delta = 0.035$ [4].
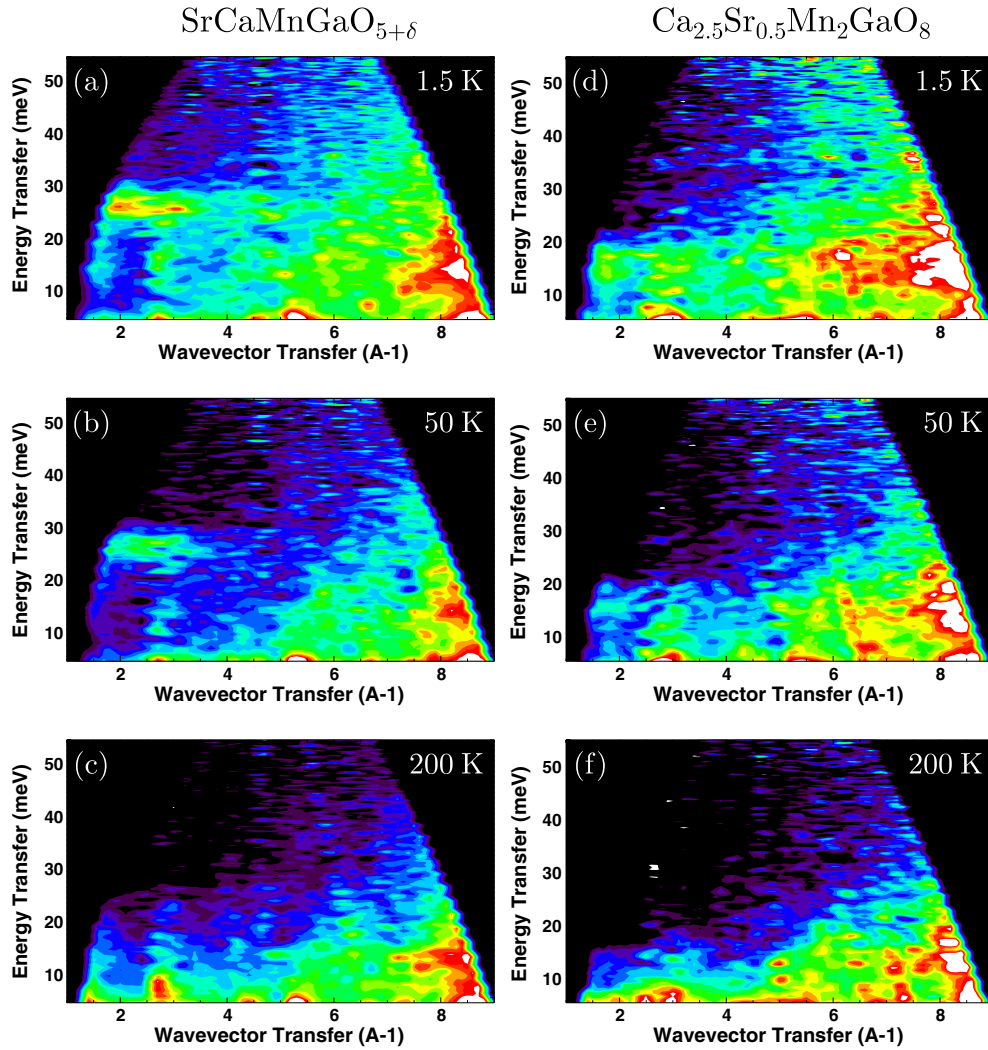
$\mathrm{SrCaMnGaO_{5+\delta}}$ $\mathrm{Ca_{2.5}Sr_{0.5}Mn_2GaO_8}$

Figure 1. Inelastic neutron scattering data for (a)–(c) $\mathrm{SrCaGaMnO_{5+\delta}}$ and (d)–(f) $\mathrm{Ca_{2.5}Sr_{0.5}Mn_2GaO_8}$. The lighter colours correspond to regions of high scattering.

magnetic form factor. This scattering can therefore be ascribed to the presence of magnon excitations in these two materials.

The development of the magnetic excitations can be seen in more detail by taking cuts at constant Q from the data shown in figure 1, and these are plotted in figure 2. The magnon mode is seen to be centred around 24 meV at 1.5 K in $\mathrm{SrCaMnGaO_{5+\delta}}$ and broadens as the temperature rises to 50 K, but at 200 K the mode has moved to lower energies to give rise to a broad quasielastic scattering (figure 2(a)). A much broader feature is seen in the constant Q scan for $\mathrm{Ca_{2.5}Sr_{0.5}Mn_2GaO_8}$, centred around 14 meV, which similarly disappears at 200 K (figure 2(b)).

The ground state magnetic structure for both compounds is known to be antiferromagnetic with the spins aligned parallel or antiparallel to the interplane direction (i.e. the spins lie perpendicular to the planes). The spin dynamics can be described using a Heisenberg
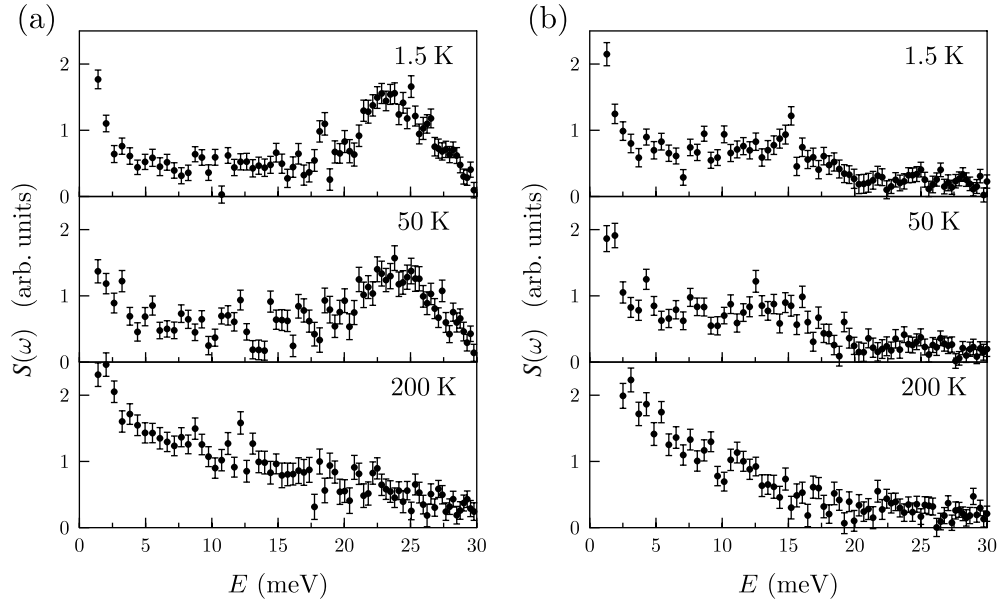
Figure 2. Neutron scattering data as a function of $Q = |\mathbf{Q}|$ obtained from figure 1 by integrating the scattering from $Q = 2.0$ to 2.5 Å^{-1} for (a) SrCaGaMnO$_{5+\delta}$ and (b) Ca$_{2.5}$Sr$_{0.5}$Mn$_2$GaO$_8$.

Hamiltonian

$$\mathcal{H} = \sum_{ij} J_\parallel \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{ij'} J_\perp^{\text{intra}} \mathbf{S}_i \cdot \mathbf{S}_{j'} - \sum_i D(S_i^z)^2, \tag{1}$$

where the first term represents nearest-neighbour coupling between Mn cations in the plane, the second term represents nearest-neighbour coupling between Mn cations in different planes of each bilayer, the third term represents the single-ion anisotropy, and the sum of exchange interactions counts each bond twice. For the single-layer material $J_\perp^{\text{intra}} = 0$ and classical spin-wave theory of the Holstein–Primakoff type leads to the dispersion relation

$$\hbar\omega_{\mathbf{Q}} = 4SJ_\parallel \left(\left[1 + \frac{D}{2J_\parallel} \right]^2 - \gamma_{\mathbf{Q}}^2 \right)^{1/2}, \tag{2}$$

where D is the single-ion anisotropy,

$$\gamma_{\mathbf{Q}} = \tfrac{1}{2}(\cos Q_x d + \cos Q_y d), \tag{3}$$

and d is the distance between nearest-neighbour spins[7]. This produces a gap at $\mathbf{Q} = (0, 0)$ and $\mathbf{Q} = (\pm\frac{\pi}{d}, \pm\frac{\pi}{d})$ of size $2S\sqrt{D^2 + 4J_\parallel D}$, which vanishes for $D = 0$.

Figures 3(a)–(c) shows this dispersion plotted for $D = 0$, demonstrating that there is a large density of states for magnetic excitations with energy $4SJ_\parallel$ corresponding to the top of the band. Our measurement averages over all directions of $\mathbf{Q}$ and the expected scattering due to this dispersion is shown schematically in figure 3(d) for the case $D = 0$. This plot includes the appropriate energy dependence from the neutron scattering cross-section, as well as the effect of the magnetic form factor for Mn^{3+}/Mn^{4+} (which reduces the scattered intensity at

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[7] For SrCaGaMnO$_{5+\delta}$, the layers are the *bc* planes and $d = \frac{1}{2}\sqrt{b^2 + c^2}$. For Ca$_{2.5}Sr_{0.5}Mn_2GaO_8$, the layers are the *ac* planes and $d = \frac{1}{2}\sqrt{a^2 + c^2}$. Our analysis assumes the spins to lie on a square lattice, although the angle at the corner of the square actually lies between 88° and 89° in both compounds, rather than being 90°.
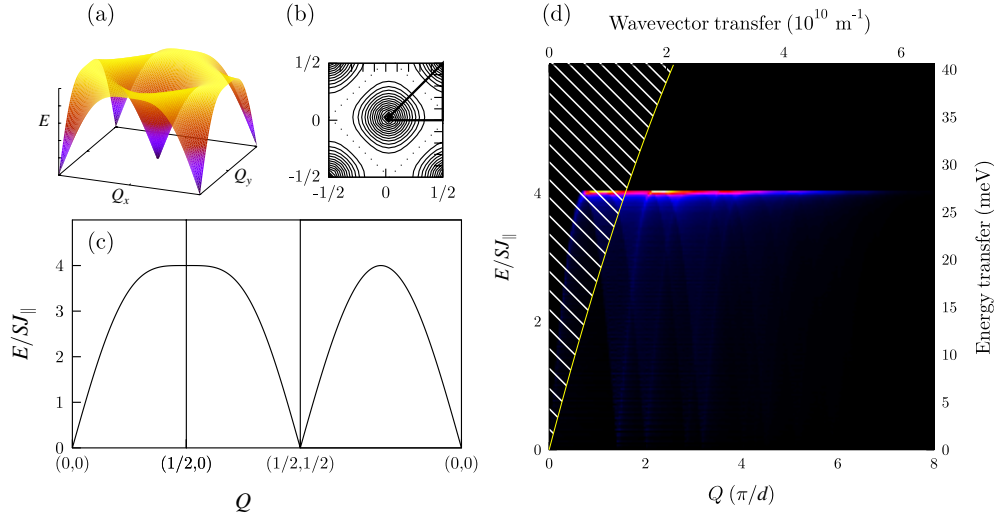
Figure 3. (a)–(c) The spin-wave dispersion is plotted as (a) an energy surface, (b) a contour map and (c) a conventional dispersion relation for the model in equation (2) for $D = 0$. (d) Schematic diagram of the expected scattering, assuming that $4SJ_\parallel = 27$ meV, which is appropriate for SrCaMnGaO$_{5+\delta}$. The shaded region in the upper left part of the graph is inaccessible in our measurement.

high-Q); this also demonstrates the strong region of scattering from the top of the magnon band.

For Ca$_{2.5}$Sr$_{0.5}$Mn$_2$GaO$_8$, the intrabilayer exchange $J_\perp^{\text{intra}}$ in equation (1) will lead to an acoustic mode (in which nearest-neighbour spins in different planes rotate together) with $\hbar\omega_{\mathbf{Q}} = 4SJ_\parallel\sqrt{1 - \gamma_{\mathbf{Q}}^2 + (J_\perp^{\text{intra}}/2J_\parallel)(1 + \gamma_{\mathbf{Q}})}$ and an optic mode (in which nearest-neighbour spins in different planes rotate in opposite directions) with $\hbar\omega_{\mathbf{Q}} = 4SJ_\parallel\sqrt{1 - \gamma_{\mathbf{Q}}^2 + (J_\perp^{\text{intra}}/2J_\parallel)(1 - \gamma_{\mathbf{Q}})}$ (see e.g. [8]). Both modes have a large density of states for magnetic excitations at the maximum energy $4SJ_\parallel + SJ_\perp^{\text{intra}}$. In both compounds, interlayer (or interbilayer) exchange $J_\perp^{\text{inter}}$ will introduce some dispersion in Q_z. Since we expect[8] that $J_\parallel \gtrsim J_\perp^{\text{intra}} \gg J_\perp^{\text{inter}}$, these effects will simply serve to broaden the scattering in energy in our measurement.

Thus we can identify the region of magnetic scattering observed in both compounds as arising from the top of the magnon bands in each case. This allows us to estimate[9] $J_\parallel = 3.4(4)$ meV for SrCaGaMnO$_{5+\delta}$, and $J_\parallel = 2.2(4)$ meV for Ca$_{2.5}$Sr$_{0.5}$Mn$_2$GaO$_8$. Since we have no way of determining the single-ion anisotropy D or the intrabilayer exchange $J_\perp^{\text{intra}}$, our estimates are upper bounds for $J_\parallel$. These values of the intraplane exchange roughly scale with the value of T_N in each compound, though T_N will be mainly controlled by the value of $J_\perp^{\text{inter}}$ which will be very small and similar in both compounds. The smaller value of $J_\parallel$ for Ca$_{2.5}$Sr$_{0.5}$Mn$_2$GaO$_8$ is in part due to the greater departure from 180° of the in-plane Mn–O–Mn bond angle [5] as compared with those in SrCaGaMnO$_{5+\delta}$ [4]. Our values of $J_\parallel$ are of the same order of magnitude as those measured in various perovskite manganites, which are in the range 1–3 meV [9–12] and in bilayer manganites, which are in the range 5–10 meV [13, 14].

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8 $J_\perp^{\text{intra}}$ is, of course, only defined for the bilayer material Ca$_{2.5}$Sr$_{0.5}$Mn$_2$GaO$_8$.
9 We assume $S = (7 - m)/2$ where m is the mean oxidation state of the Mn ions; formally $m = 3 + 2\delta$ for SrCaGaMnO$_{5+\delta}$ and $m = \frac{7}{2}$ for Ca$_{2.5}$Sr$_{0.5}$Mn$_2$GaO$_8$.

We tentatively assign the extra broadening of magnetic excitations in $Ca_{2.5}Sr_{0.5}Mn_2GaO_8$ to the presence of the two magnon branches that cannot be separately resolved.

Acknowledgments

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