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# One-dimensional ferromagnetism of gaudefroyite $Ca_4(MnO)_3(BO_3)_3CO_3$

R. K. Li[1,2] and C. Greaves[1]
[1]*School of Chemical Sciences, The University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom*
[2]*Beijing Center of Crystal Research and Development, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100080, China*

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The structure of gaudefroyite, $Ca_4(MnO)_3(BO_3)_3CO_3$, is built up of linear chains of edge-shared $MnO_6$ octahedra which are interconnected via $BO_3$ groups to form a Kagomé lattice in the *ab* plane. Magnetic measurements show that the Mn moments along the chain are ferromagnetically coupled, but frustration exists between the chains because of the triangular arrangement of the Mn ions within the *ab* plane. Over a large temperature range, $10\text{ K} \leqslant T \leqslant 320\text{ K}$, the magnetic properties of this compound can be described by the classical Heisenberg spin chain model with a single ion anisotropy modification, $H=-2J\Sigma S_iS_{i+1}+D\Sigma S_{iz}^2$, with $J=4.2\text{ K}$ and $D=0.67\text{ K}$. Below 10 K, the moments are effectively constrained to the *ab* plane and the magnetization with $H_0 \| ab$ shows spin glass behavior. No indication of magnetic ordering has been observed down to 1.8 K.

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Low-dimensional magnetic systems have been the focus of both theoretical and experimental studies for nearly half a century.[1] For one dimensional (1D) systems, exact solutions exist for some model Hamiltonians and a large number of extended inorganic and molecular compounds containing 1D magnetic chains have been reported,[2,3] which allows a direct comparison between theoretical and experimental results. For an isotropic Heisenberg chain, Fisher has obtained an exact solution for the $S=\infty$ limit,[4] and for the strong anisotropic Ising system, exact solutions exist for the spin quantum numbers $S=\frac{1}{2},1,\frac{3}{2}$, and $\infty$.[5–8] It has also been proposed[9] and observed,[10] in $CsNiF_3$, that 1D ferromagnetic chains can host nonlinear excitations, i.e., magnetic solitons, as the moving of domain walls. Experimentally, many compounds exhibit antiferromagnetic (AFM) ordering along the chain while relatively few ferromagnetic (FM) chains are realized in real systems.[2,3] $Mn^{3+}$ containing oxides frequently exhibit Jahn-Teller distortions, and when doped to produce mixed $Mn^{3+}/Mn^{4+}$ compounds, double exchange[11] can provide ferromagnetism as in the colossal magnetoresistive (CMR) materials of three-dimensional (3D) $(La,Sr)MnO_3$ and two-dimensional (2D) layered $LaSr_2Mn_2O_7$ systems.[12] Two recent reports, on $PbMnBO_4$ by Park *et al.*,[13] and $YCa_3(MnO)_3(BO_3)_4$ (YCMBO) by the present authors,[14] suggested that the chains of $Mn^{3+}$ ions in these systems are FM. This has encouraged us to focus attention on the mineral gaudefroyite itself, which the YCMBO compound is derived from, and therefore contains similar chains of linked $MnO_6$ octahedra.

Gaudefroyite, $Ca_4(MnO)_3(BO_3)_3CO_3$, from the Tashgagalt mine, Morocco, was first reported by Jouravsky and Permingeat.[15] Its structure [Fig. 1(a)] was subsequently determined by Granger and Protas[16] and refined by Yakubovich *et al.*[17] and Hoffmann *et al.*,[18] in space group $P6_3$ or $P6_3/m$, respectively. The structure comprises edge-shared $MnO_6$ octahedra which form 1D chains along [001]. Due to the Jahn-Teller distortion of the $Mn^{3+}$ ions, the uneven Mn-O bonds lead to a slightly zigzag chain. The chains are over 5 Å apart and are interlinked by $BO_3$ groups to produce a 2D Kagomé net in the *ab* plane. Two distinct types of channels are formed in the net: one larger apatitelike hexagonal channel accommodates six $Ca^{2+}$ ions and two $CO_3{}^{2-}$ groups per unit cell; two smaller trigonal channels are occupied solely by one $Ca^{2+}$ ion each. Our previous study demonstrated that the $CO_3{}^{2-}$ group in gaudefroyite, $Ca_4(MnO)_3(BO_3)_3CO_3$, can be replaced by another $BO_3{}^{3-}$ group, with one $Ca^{2+}$ ion simultaneously being substituted by a $Y^{3+}$ ion to provide charge balance and give $YCa_3(MnO)_3(BO_3)_4$. Neutron diffraction and magnetic measurements proved that the $Mn^{3+}$ ions in the synthetic analog YCMBO experience FM intrachain exchange. The chains are AFM coupled within the *ab* plane and order below 7.5 K into a $q=0$ Kagomé type magnetic structure [Fig. 1(b)]. In addition to the inherent interest of studying the properties of such FM chains, the ordering mechanism in Kagomé systems remains in dispute, and suggestions include order by disorder,[19] dipole-dipole or next-next-neighbor interactions.[20] It is therefore important to determine whether the ordering in the *ab* plane is also present in the nondisordered A site gaudefroyite, which contains only $Ca^{2+}$ ions in the structural channels, and the magnetic properties of a single crystal of this material are reported here.

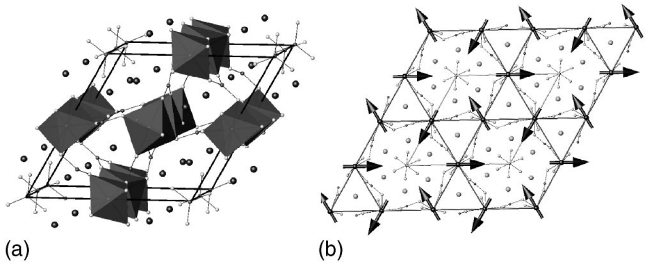

FIG. 1. The crystal structure of gaudefroyite, $Ca_4(MnO)_3(BO_3)_3CO_3$, (a), showing the $MnO_6$ chains in the unit cell, and (b), showing the $q=0$ Kagomé-type magnetic structure of the *ab* plane found in its synthetic analog, $YCa_3(MnO)_3(BO_3)_4$; along *c* all moments are parallel.

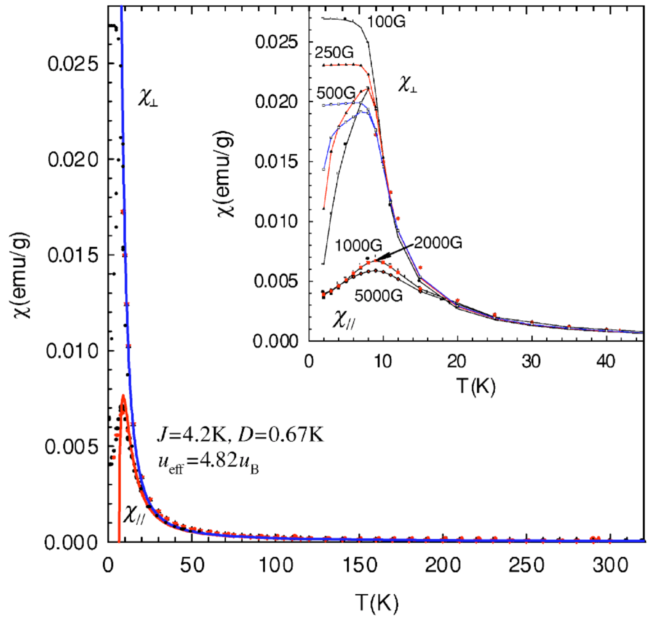

FIG. 2. (Color online) Magnetic susceptibility of gaudefroyite crystal. The lines in the main figure are the fit using Eqs. (1) and (2). The lines in the inset provide only a guide for the eye.

Our sample of gaudefroyite originated from N'chwaning mine II in the Kalahari manganese field, Hotazel, Kuruman, Cape Province, South Africa. A black shiny crystal of approximate size $2.5\times1.5\times3.5\ \mathrm{mm}^3$ (with the longer dimension parallel to the $c$ axis) was selected for the magnetic measurements. A smaller separate crystal was crushed to check phase purity by powder x-ray diffraction (XRD). The magnetic measurements were performed on a Quantum Design PPMS magnetometer. For the measurements of parallel or perpendicular magnetization of the sample, the crystal was fixed to the sample holder with the $c$ axis aligned parallel to or perpendicular to the direction of the magnetic field.

Rietveld refinement of the XRD pattern of gaudefroyite using the GSAS package[21] and starting with the reported structural parameters in space group $P6_3/m$ quickly converged to $R_{wp}=1.84\%$ and $\chi^2=1.161$. The good agreement between the calculated and observed pattern confirmed that the crystals are free from contamination by other codeposited minerals; in particular, all the diffraction peaks could be indexed on the hexagonal cell of $a=10.6046(1)$ Å, and $c=5.8858(1)$ Å, and there are no residual peaks in the difference plot. The refined structural parameters are in good agreement with Refs. 17 and 18.

The magnetic susceptibility of the crystal shows strong anisotropy below 20 K (Fig. 2). The susceptibility along $c$ ($\chi_{\parallel}$) shows a peak around 9.5 K, whereas that perpendicular to $c$ ($\chi_{\perp}$) continues to grow and shows typical FM behavior. Curie-Weiss analysis of the magnetic susceptibilities gives a positive $\theta$ (+45 K), also indicating FM interaction. However, divergence of the fit already occurs about 100 K, well above the transition. We therefore tried to use the Heisenberg spin chain model to fit the experimental data. The expressions for the extension of the Fisher model[4] to include single ion anisotropy were given by Smith and Friedberg.[22] For a classic spin with spin number $S$ in a magnetic field $\mathrm{H}_0$:

$$H=-2JS(S+1)s_i\cdot s_{i+1}+DS(S+1)s_{iz}^2 \\ -g\mu_B[S(S+1)]^{1/2}\mathrm{H}_0\cdot s_i$$

such that

$$\chi_{\parallel}=\chi_0-4/15\chi_c[DS(S+1)/kT]F, \qquad (1)$$

$$\chi_{\perp}=\chi_0+2/15\chi_c[DS(S+1)/kT]F, \qquad (2)$$

with

$$\chi_0=\frac{Ng^2S(S+1)\mu_B^2}{3kT}\frac{1+u}{1-u},$$

$$F=\frac{(1+u)(1+v)}{(1-u)(1-v)}+\frac{2u}{1-u},$$

$$u=\coth[2JS(S+1)/kT]-kT/[2JS(S+1)],$$

$$v=1-[3ukT/2JS(S+1)],\ \chi_c=Ng^2\mu_B^2S(S+1)/3kT.$$

Using these expressions and a single set of parameters of $J=4.2$ K, $D=0.67$ K, and $\mu_{\mathrm{eff}}=4.82\ \mu_B$, we can fit both $\chi_{\parallel}$ and $\chi_{\perp}$ in the temperature range $10\ \mathrm{K}\leqslant T\leqslant 320$ K with good agreement (Fig. 2). In addition, the peak at 9.5 K in $\chi_{\parallel}$ is also reproduced, which means it originates entirely from the single ion anisotropy and is not indicative of AFM order. Both positive values obtained for $J$ and $D$ mean that along the chain the spins are FM coupled and the spins are preferentially oriented in the $ab$ plane, which is also consistent with the magnetic structure determined for its synthetic analog, YCMBO.[14]

Below 10 K, $\chi_{\parallel}$ shows a small field-dependence and no observable differences in field-cooled (FC) and zero-field-cooled (ZFC) measurements, whereas FC and ZFC measured susceptibilities in the $ab$ plane ($\chi_{\perp}$) diverge, and the ZFC value decreases below 9 K (Fig. 2, inset). $\chi_{\perp}$ also shows a strong field dependence, with sharper peaks at lower fields for ZFC measurements, and $\chi_{\perp}$ in FC measurements saturates to different values with different applied fields. All the above facts point to a typical spin glass behavior.[23] The spin glass state in the $ab$ plane is also supported by a measurement of time decay of the remanent magnetization at 1.8 K (Fig. 3, inset).

The field-dependent magnetization measured at 2 K is shown in Fig. 3. When the magnetic field is in the $ab$ plane, the magnetization sharply increases to give ~80% of its ideal value ($4\mu_B$) below 1 T; along $c$, however, the magnetization changes slope at around 1 T and approaches saturation only for $H_0>3$ T. The saturated moments in the $ab$ and $c$ directions at 7 T are $3.77\mu_B/\mathrm{Mn}$ and $3.82\mu_B/\mathrm{Mn}$, respectively, which are very close to the ideal value, indicating that all the $\mathrm{Mn}^{3+}$ moments are aligned in the magnetic field direction. The saturated moment is also nearly identical to that of its synthetic analog ($3.83\mu_B/\mathrm{Mn}$), YCMBO, which means that there is probably no other substituted impurities in the Mn sites of the gaudefroyite crystal studied. The different magnetization behavior in the $ab$ and $c$ directions originates

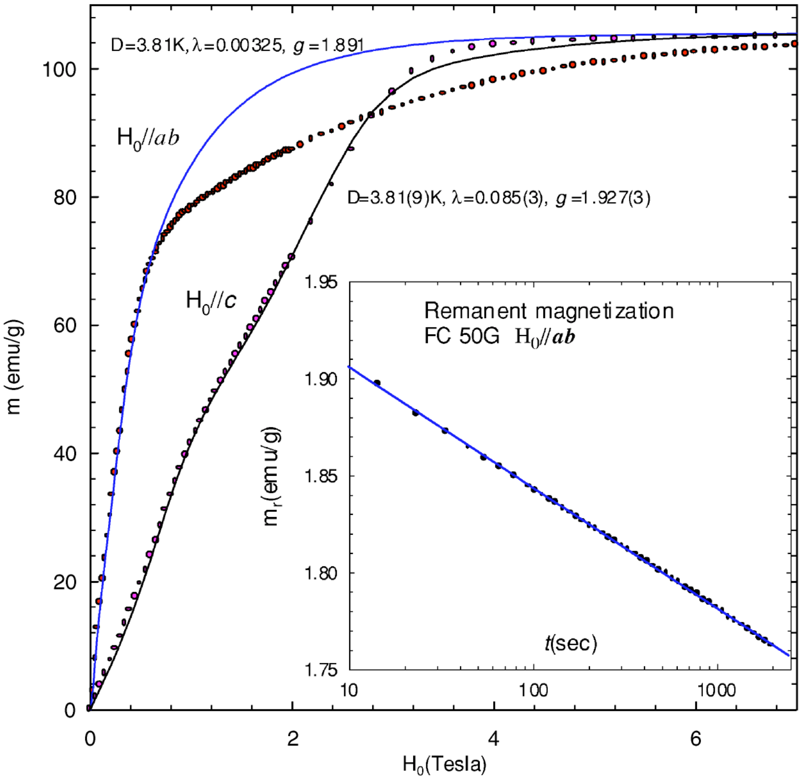

FIG. 3. (Color online) Magnetization at 2 K of the gaudefroyite crystal. The inset shows the time-dependent magnetization at 1.8 K.

from the anisotropy. Making the crude approximation that full alignment of the Mn moments is achieved at 7 T, one obtains $\Delta g = g_{\parallel} - g_{\perp} = 0.027$ and therefore, $D = (\lambda/2)\Delta g = 1.7$ K, taking $\lambda = \xi/2S$ and $\xi = 355\ \mathrm{cm}^{-1}$.

The zero-field splitting parameter $D$ can also be obtained from the low-temperature magnetization.[24] When the magnetic field is parallel to $c$, we can use a mean field treatment for the system:

$$H = -2zJ\langle S\rangle S_{iz} + DS_{iz}^2 - g\mu_B \mathrm{H}_0 \cdot S_{iz}.$$

$z$ is the coordination number of the interacting $\mathrm{Mn}^{3+}$ ions, for which $S=2$, so that

$$M = M_0 \frac{e^h - e^{-h} + 2e^{-3d+2h} - 2e^{-3d-2h}}{e^d + e^h + e^{-h} + e^{-3d+2h} + e^{-3d-2h}} \tag{3}$$

with $d = D/kT$, $h = g\mu_B H_{\mathrm{eff}}/kT$, $H_{\mathrm{eff}} = \mathrm{H}_0 + \lambda M$, and $\lambda = 2zJ/Ng^2\mu_B^2$.

The fit using Eq. (3) with $D=3.81(9)$ K, $J=3.1(1)$ K, and $M_0 = 3.854(6)\mu_B$ (we neglect the interchain interaction and take $z=2$) to the magnetization curve along the $c$ direction successfully reproduces the change of slope and gives a reasonable agreement throughout the whole field range (0–7 T). It should be noted that the value of $D$ here is significantly larger than that previously obtained from the high temperature susceptibility. The discrepancy probably has two origins. First, the Fisher chain model is 1D and is exact at high temperatures, whereas the low-temperature magnetization calculation we adopted is essentially a mean field 3D approximation. Second, at low temperatures inter-chain interactions cannot be ignored and will enhance the effects of the anisotropy.[25] The obtained zero-field splitting parameter $D$ can be compared to those obtained from electron paramagnetic resonance (EPR) measurements on similar compounds.[26] Only very recently, by using high field and high frequency, has the EPR spectrum of $\mathrm{Mn}^{3+}$ in octahedral coordination been observed.[27–29] The obtained $D$ values range from 1 to $4.5\ \mathrm{cm}^{-1}$, equivalent to 1.5 to 6.5 K, which are not far from our obtained $D$ values.

For the magnetic field in $ab$ plane, the following Hamiltonian

$$H = -2zJ\langle S\rangle S_{iz} + DS_{iz}^2 - \tfrac{1}{2} g\mu_B \mathrm{H}_0 \cdot (S_+ + S_-)$$

can be diagonalized[30] to give energy levels

$$E_1 = \tfrac{5}{6}D + \left(\tfrac{9}{4}D^2 + h^2\right)^{1/2},$$

$$E_2 = \tfrac{5}{6}D - \left(\tfrac{9}{4}D^2 + h^2\right)^{1/2},$$

$$E_3 = 2P^{1/2}\cos(\theta/3),$$

$$E_4 = 2P^{1/2}\cos(\theta/3 + 2\pi/3),$$

$$E_5 = 2P^{1/2}\cos(\theta/3 - 2\pi/3).$$

with $P = \frac{13}{9}D^2 + \frac{4}{3}h^2$, $\cos\theta = \left(\frac{35}{27}D^3 - \frac{8}{3}Dh^2\right)/P^{3/2}$, and $h = g\mu_B(\mathrm{H}_0 + \lambda M)$.

Using the equation

$$M = N\frac{\sum_{i=1}^{5}(-\partial E_i/\partial \mathrm{H}_0)e^{-E_i/kT}}{\sum_{i=1}^{5} e^{-E_i/kT}}$$

and $D=3.81$ K and $J=1.4$ K, we can calculate the magnetization curve for $\mathrm{H}_0 \parallel ab$, which gives good agreement at low field but at higher field the agreement is worse (Fig. 3). The tentative explanation for this is that the Mn site in the crystal does not have $P6_3/m$ symmetry but an approximate point symmetry of *mmm*, with 3 pairs of different Mn-O bonds: Mn-O1, 1.856(5) Å; Mn-O2, 2.226(7) Å; and Mn-O3, 1.964(6) Å. Therefore the anisotropy of individual Mn ions in the *ab* plane probably cannot be ignored. The in-plane anisotropy of a less distorted Mn-O environment in $CsMn(SO_4)_2 \cdot 12D_2O$ was obtained from both inelastic neutron scattering[31] and high-field EPR[29] with $E=0.272\ cm^{-1} = 0.4$ K or $E=0.245\ cm^{-1}=0.35$ K. Also, the *c* axis (along the elongated bonds Mn-O2) of the distorted $MnO_6$ octahedron is not in coincidence with the crystallographic *c* axis but tilted 48° off the *c* direction; in this case there will also be a contribution from the $S_z$ moment to the *ab* plane. Since the diagonalization of the general form Hamiltonian has not been worked out in closed form, we made no further effort to improve the fit.

The geometries of the $MnO_6$ chains in gaudefroyite, YCMBO, and $PbMnBO_4$ are nearly identical, and all of them support FM along the chain. However, as previously pointed out,[13,14] magnetic interactions in other Mn compounds with similar bond geometries give AFM order. The FM interaction observed in these 1D chains may relate to the superexchange through the near 90° Mn-O-Mn bonds, which are at angles of 104.9(4)° and 82.8(3)° in gaudefroyite, 102.4° and 83.5° in YCMBO, 104.0° and 83.8° in $PbMnBO_4$, and may also have something to do with the borate group.[32] Within the *ab* plane, theory predicts that the Kagomé lattice has a disordered magnetic ground state. The observation of $q=0$ order in YCMBO but not in gaudefroyite seems to support the reports on jarosite that lattice disorder enhances magnetic order[33] since in YCMBO there is significant disorder in the randomly occupied Ca/Y sites. However, whereas in jarosite the lattice disorder is at the magnetic sites, in YCMBO the disorder is at Ca/Y sites, leaving the magnetic lattice intact. A recent report based on magnetic measurement on pure iron jarosites[34] also contradicts with the proposed disordered ground state. Further experiments in the future are needed to address the influence of disorder on nonmagnetic sublattices to magnetic ordering phenomena in this type of system.

In conclusion, the $MnO_6$ chain in gaudefroyite can be modeled by a Heisenberg classical spin chain with an anisotropy modification, $H=-2J\Sigma S_i S_{i+1} + D\Sigma S_{iz}^2$, with $J=4.2$ K and $D=0.67$ K. Within the *ab* plane, as a consequence of frustration from the Kagomé lattice arrangement of the FM chains, no 3D magnetic order has been observed among the chains that remain as spin glass down to 1.8 K.

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