Magnetic properties of the coupled ladder system MgV$_2$O$_5$

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We present magnetic susceptibility measurements on MgV$_2$O$_5$, a compound in which the vanadium oxide planes have the same topology as in CaV$_2$O$_5$. The most striking property is that there is an energy gap of about 15 K, much smaller than in CaV$_2$O$_5$, where the values reported are of the order of 500 K. We show that this may be understood naturally in terms of the phase diagram of the frustrated, coupled ladder system. This analysis leads to the prediction that MgV$_2$O$_5$ should have incommensurate dynamic spin fluctuations.

Materials which could be used to probe other regions of the rather rich phase diagram of Ref. $^6$ would be very welcome.

In this paper, we present magnetic susceptibility measurements for another member of the vanadate family with the same topology, namely MgV$_2$O$_5$. This system is quite intriguing because, although the vanadium oxide planes are very similar to those in CaV$_2$O$_5$, the magnetic properties are strikingly different, with, in particular, a spin gap of only 15 K. As we shall argue below, this difference may be attributed to the presence of a helical ordered phase in the phase diagram of the model of Fig. 1, thus lending further support to the results of Ref. $^3$.

MgV$_2$O$_5$ was prepared by solid state reaction, starting from a mixture of MgO and VO$_2$, according to the procedure described in Ref. $^5$, and its structure was determined from x-ray powder diffraction Rietveld analysis $^7$. It crystallizes in the orthorhombic system of space group Cmcm with, at 294 K, $a = 3.6913(2)$Å, $b = 9.9710(4)$Å, and $c = 11.0173(4)$Å. The structure retains the basic framework of the V$_2$O$_5$ host lattice, which is built up in one direction by infinite double lines of VO$_5$ square pyramids joined by alternate sharing of edges and corners to form vanadium zigzag chains along the $a$ axis, and held together by corner sharing in the [001] direction. It is therefore indeed analogous to the structure of the compounds $\alpha$′-NaV$_2$O$_5$ $^8$ and CaV$_2$O$_5$ $^9$. A peculiar feature of the MgV$_2$O$_5$ structure is the shift by $a/2$ along [100] for alternate layers (doubling of the short inter-layer parameter), and the puckering of the V$_2$O$_5$ layers (angle $\mu = 21^\circ$) to accommodate Mg ions in tetrahedral coordination. An idealized view of the structure viewed down the $a$ axis is presented in Fig. 2. As for CaV$_2$O$_5$, MgV$_2$O$_5$ is a monovalent (V$^{4+}$) oxide, and vanadium atoms are located on a single crystallographic...
Magnetic susceptibility measurements were performed using a superconducting quantum interference device QUANTUM DESIGN SQUID susceptometer. The magnetic field induction was 1kG. The molar susceptibility was corrected for diamagnetism by using Pascal’s constants. The raw data are presented in Fig. 3. These data were reproduced on three different samples, with, however, a large variation of the temperature-independent background from sample to sample. The main features of these data are: i) a regular increase between 400 K and 100 K; ii) a small, not fully reproducible bump around 85 K; iii) a very slow decrease between 70 K and 15 K; iv) a much faster decrease down to 4 K; v) a very fast increase at lower temperature.

The low-temperature data are typical of a system with a spin gap. We have thus performed a fit of the data between 2 K and 25 K with the formula

$$\chi(T) = A + B/T + (C/\sqrt{T}) \exp(-\Delta/T),$$

where \(A\) includes all temperature-independent contributions (Van Vleck, plus possible contributions from impurity phases with temperature-independent susceptibility in this range), \(B/T\) accounts for paramagnetic impurities, and \((C/\sqrt{T}) \exp(-\Delta/T)\) describes the susceptibility of a one-dimensional system with a gap $\Delta$. The fit is depicted in the inset of Fig. 3, and the parameters used are $A = 1.71 \times 10^{-3}$ emu/mole, $B = 1.16 \times 10^{-2}$ emuK/mole, $C = 7.82 \times 10^{-3}$ emuK$^{1/2}$/mole and $\Delta = 14.8$ K. The fit is very accurate, with a residue of only $1.6 \times 10^{-6}$ over a temperature range 2 - 25 K. We have also tried to fit the data with a term of the form $C \exp(-\Delta/T)$ typical of gapped, two-dimensional systems $\Delta$. The result was clearly not as good, which we take to indicate the effective one-dimensionality of the system, or that MgV$_2$O$_5$ remains in the limit of weakly interacting ladders.

While further investigation of this system, for example by Nuclear Magnetic Resonance, would be very useful to confirm these results, the presence of a rather small gap ($\approx 15$ K) as compared to CaV$_2$O$_5$ ($\approx 500$ K) is clearly very interesting. We believe that this result can be understood in terms of the model of Fig. 1, due to modest but not negligible differences in the structural parameters leading to important differences in the exchange integrals. The direct determination of exchange integrals for a particular system is a very difficult task, because it requires an accurate fit of the temperature-dependence of the susceptibility over a large temperature range. In vanadates this has been possible only in two cases for which we have a good theoretical understanding of the temperature-dependence of the susceptibility of the underlying model, $\alpha'$-NaV$_2$O$_5$ $\Delta$, and CsV$_2$O$_5$ $\Delta$. $\alpha'$-NaV$_2$O$_5$ is a one-dimensional Heisenberg chain of corner-sharing VO$_5$ pyramids with a single exchange integral $J_2$(NaV$_2$O$_5$). The susceptibility of this model is known very accurately from the work of many authors $\Delta$, and a fit of the experimental susceptibility gives $J_2$(NaV$_2$O$_5$) $\approx 530$ K. CsV$_2$O$_5$ consists of weakly interacting pairs of edge-sharing pyramids. The relevant model is a Heisenberg model with only two spins coupled by an exchange integral $J_1$(CsV$_2$O$_5$). The susceptibility can be calculated analytically, and a fit to the experimental results gave $J_1$(CsV$_2$O$_5$) $\approx 146$ K $\Delta$.

To obtain estimates of the exchange integrals in other members of the family, we make the reasonable assumption that these depend only on the local geometry of the bonds. For corner-sharing pyramids ($J_2$, $J'_2$), the dominant process is superexchange, and the exchange integrals are expected to depend on the local parameters defined in Fig. 4 according to $\Delta$.

$$J_2(d, \theta), J'_2(d, \theta) \propto \cos^4(\theta)d^{-14},$$

where $\Delta$ is the vanadium-vanadium distance. Having no other, more direct source of information at hand for vanadates, we will use these dependences in the following. The results for the exchange integrals of CaV$_2$O$_5$ and MgV$_2$O$_5$ based on the most accurate structural information available for $\alpha'$-NaV$_2$O$_5$ $\Delta$, CsV$_2$O$_5$ $\Delta$, CaV$_2$O$_5$ $\Delta$ and MgV$_2$O$_5$ $\Delta$ are given in Table I. The trend is quite clear: $J_1$ is larger for MgV$_2$O$_5$ than for CaV$_2$O$_5$, while $J'_2$ is considerably smaller, so that the ratio $J'_2/J_1$ is approximately 4.3 for CaV$_2$O$_5$, but only 2.5 for MgV$_2$O$_5$. According to the analysis of the model performed in Ref. $\Delta$, this ratio is a very important parameter: $J'_2/J_1 = 4.3$ clearly puts CaV$_2$O$_5$ in the ladder limit with a large gap $\Delta$. However, $J'_2/J_1 = 2.5$ with $J'/J_1 = 2.8$ puts MgV$_2$O$_5$ very close to the helical ordered - hence gapless - phase according to the phase diagram obtained by Schwenger boson mean-field theory $\Delta$. The system is thus expected to have a very small gap, as this vanishes continuously at the boundary. Of course, estimates based on Eqs. (3) and (4) are not very accurate $\Delta$, but the conclusions can be expected to remain qualitatively correct as long as the exchange integrals depend strongly on the distances, which has indeed been found to be the case in insulating oxides $\Delta$. An interesting consequence of the proximity to a helical ordered phase is that MgV$_2$O$_5$ should exhibit incommensurate dynamic spin fluctuations. We do not present calculations to elaborate on this point here. This prediction could be verified by inelastic neutron scattering when single crystals of sufficient sizes become available.

Let us now turn to the high-temperature data. The increase of susceptibility with decreasing temperature, showing a maximum at intermediate temperatures, is
typical of systems with antiferromagnetic exchanges. Fitting the measured curve with a Heisenberg model has proven to be as difficult here as for other members of the family. The problem of the peak occurring well below the energy scale of the interactions may be due to poor theoretical estimates of the temperature dependence for frustrated systems with dynamic helical fluctuations. Work is in progress in this direction.

We focus finally on the broad susceptibility peak which occurs around 85 K. To address the possibility that this behavior is related to structural modifications, we have studied the thermal evolution of the x-ray diffractograms. X-ray powder patterns were collected up to θ = 30° (except the diffractogram at 83 K which was collected up to 75° in order to perform a Rietveld refinement) in a high-accuracy MICROCONTROLE diffractometer, using CuKα radiation (graphite monochromator) from an 18kW rotating-anode generator and a flowing cryostat with a stability range of 0.5 K. The thermal variation of the cell parameters, determined by least-squares refinement, is presented in Fig. 5. The lattice parameter a along the vanadium chains increases slightly from 170 K to 100 K, a temperature at which the fluctuations in the data suggest that a structural instability may be occurring, then decreases monotonically from 65 K to 8 K. Interestingly, the instability temperature range 100-65 K corresponds to the maximum observed in the susceptibility curve. Moreover, a shortening of the lattice parameter a is qualitatively consistent with an increase of the exchange integrals $J_1$ and $J_2$, hence with the experimental decrease of the susceptibility. However, it is difficult to correlate this with a structural modification because we did not observe a notable change on the Rietveld refinement of the structure performed at 83 K.

The interlayer distance b decreases continuously over the whole temperature range, while c presents no clear evolution. A structural determination at low temperatures (around 4 K) would be very useful, and we plan to perform this in the near future by neutron powder diffraction.

To summarize, the magnetic susceptibility data reported in this paper suggest that MgV$_2$O$_5$ is a new spin gap system with a gap of about 15 K. This very small value should be contrasted with the much larger value (≥500 K) reported for CaV$_2$O$_5$. We have shown that this difference can be understood in terms of the frustrated, coupled ladder system due to the proximity to an ordered helical phase in the case of MgV$_2$O$_5$. This interpretation suggests that MgV$_2$O$_5$ should have incommensurate dynamic spin fluctuations, a prediction which could be tested by inelastic neutron scattering as soon as suitably large crystals are available. Given the potential interest of systems with spin gaps in the range 0-30 K for studies under magnetic field, the magnetic properties of this system are likely to become a very active field of research.

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| Material       | $d_{V-O}$ | $d_{O}^-$ | $d(J_2)$ | $d(J_2')$ | $J_2$ | $J_2'/J_1$ | $J_2'/J_2$ |
|----------------|-----------|-----------|-----------|-----------|------|------------|-----------|
| CsV$_2$O$_5$   | 3.073     | 146       | 0.698     | 1.962     | 530  |            |            |
| α'-NaV$_2$O$_5$| 3.025     | 170       | 0.648     | 1.949     | 1.905| 587 730    | 3.5 4.3    |
| CaV$_2$O$_5$   | 3.257     | 201       | 0.666     | 1.954     | 1.975| 565 511    | 2.8 2.5    |

**TABLE I.** Structural parameters and measured or estimated exchange integrals of CaV$_2$O$_5$, α'-NaV$_2$O$_5$, CsV$_2$O$_5$ and MgV$_2$O$_5$. Distances are in Å, and exchange integrals are in Kelvin.
FIG. 1. Schematic representation of the frustrated coupled ladder system with one type of nearest neighbour exchange integral \((J_1)\) and two types of next nearest neighbour exchange integrals \((J_2, J'_2)\).

FIG. 2. Idealized structure of MgV\(_2\)O\(_5\) viewed down the a axis (3.69Å).

FIG. 3. Thermal variation of the molar magnetic susceptibility of MgV\(_2\)O\(_5\). Diamonds: experimental points. Inset: enlargement of the low-temperature region with fit (solid line) to Eq. (2).

FIG. 4. a) V-3d and O-2p orbitals involved in superexchange between corner-sharing VO\(_5\) square pyramids; b) basic parameters of the VO\(_5\) square pyramid.

FIG. 5. Temperature dependence of lattice constants for MgV\(_2\)O\(_5\). Triangles and black dots correspond to two successive collection sets. The open circles correspond to the Rietveld refinement at 83 K.