Magnetic phase diagrams of the Kagomé staircase compounds $\text{Co}_3\text{V}_2\text{O}_8$ and $\text{Ni}_3\text{V}_2\text{O}_8$

N R Wilson, O A Petrenko and G Balakrishnan

Department of Physics, University of Warwick, Coventry CV4 7AL, UK

E-mail: nicola.r.wilson@warwick.ac.uk

Received 5 September 2006
Published 23 March 2007
Online at stacks.iop.org/JPhysCM/19/145257

Abstract

An extensive low temperature magnetization study of high quality single crystals of the Kagomé staircase compounds $\text{Ni}_3\text{V}_2\text{O}_8$ and $\text{Co}_3\text{V}_2\text{O}_8$ has been performed, and the $H$–$T$ phase diagrams have been determined from these measurements. The magnetization and susceptibility curves for $\text{Co}_3\text{V}_2\text{O}_8$ are analysed in terms of their compatibility with the different ferromagnetic and antiferromagnetic structures proposed for this compound. For $\text{Ni}_3\text{V}_2\text{O}_8$, the phase diagram is extended to magnetic fields higher than previously reported; for a field applied along the $a$ axis, the low temperature incommensurate phase is found to close at around 90 kOe.

1. Introduction

The magnetic effects caused by the Kagomé type lattice have interested theorists and experimentalists for many years. The two dimensional layers of corner sharing triangles possess macroscopic degeneracy when each vertex is occupied by a Heisenberg spin interacting antiferromagnetically with its nearest neighbours. This causes a high degree of magnetic frustration and the system remains a disordered spin liquid down to zero temperature.

Samples that possess a perfect form of this structure are difficult to find, and so experimentalists are turning to structures with variations of the Kagomé lattice. The Kagomé staircase systems $\text{M}_3\text{V}_2\text{O}_8$ [1, 2] with $\text{M} = \text{Ni, Co or Cu}$ have a structure of magnetic atoms that is based on the Kagomé lattice. Their structure is different in that the layers are not two dimensional but are buckled in and out of the plane. This variation means that the symmetry of the system is reduced and further neighbour interactions are much more significant. These changes partially relieve the frustration and allow long-range order to be established.

The magnetic properties of $\text{Ni}_3\text{V}_2\text{O}_8$ have been characterized using magnetization, specific heat and neutron diffraction techniques [3, 4]. The system passes from a paramagnetic phase to a high temperature incommensurate phase at 9.1 K. The next transition is at 6.3 K where the system enters a low temperature incommensurate phase. At 3.9 K the system then enters a commensurate phase with remnant structures, then finally a purely commensurate
antiferromagnetic phase below 2 K. An additional interest in Ni$_3$V$_2$O$_8$ is associated with
the low-temperature ferroelectricity observed in this compound [5] and the related complex
behaviour caused by the magnetoelectric interactions [4].

It has been suggested that the Co system passes through similar phase transitions [6], but
our recent neutron powder diffraction study has shown otherwise [7]. At 11 K, Co$_3$V$_2$O$_8$ moves
from a paramagnetic state to an incommensurate antiferromagnetic state. At 6 K there is a
transition to a ferromagnetic state, in which the system remains down to the lowest temperature
studied of 1.7 K. The Curie–Weiss temperature for this system is approximately 15 K. Here,
we present the temperature and field dependence of the magnetization measured in the various
magnetic phases of both compounds for different directions of applied magnetic field. For
Co$_3$V$_2$O$_8$, the magnetic phase diagram is presented here for the first time and for Ni$_3$V$_2$O$_8$, a
new phase boundary is shown.

2. Experimental details

The Kagomé staircase compounds Ni$_3$V$_2$O$_8$ and Co$_3$V$_2$O$_8$, where Ni has $S = 1$ and Co
has $S = 3/2$, have the space group Cmca with lattice parameters [8] $a = 5.936(4)$ Å, $b = 11.420(6)$ Å and $c = 8.240(5)$ Å for Ni$_3$V$_2$O$_8$ and $a = 6.030(4)$ Å, $b = 11.486(2)$ Å
and $c = 8.312(5)$ Å for Co$_3$V$_2$O$_8$. The atoms form layers of edge-sharing MO$_6$ octahedra,
separated by non-magnetic VO$_4$ tetrahedra. The samples were prepared using the floating zone
technique previously described [9]. Single crystals of both samples of approximately 2 cm$^3$ in
volume were produced with mosaic spreads of less than 1°. An Oxford Instruments Vibrating
Sample Magnetometer (VSM) and a Quantum Design SQUID magnetometer were used to
measure the temperature and field dependence of the magnetization in these compounds. The
samples were investigated with fields applied along each of the three main crystallographic
directions, aligned with an accuracy of at least 3°. The phase transitions were tracked in the
temperature interval between 1.4 and 12 K in a magnetic field range of up to ±120 kOe.

3. Results and discussion

A range of characteristic magnetization and susceptibility curves measured in Co$_3$V$_2$O$_8$ is
shown in figure 1. The $M(H)$ curve for a field applied along the easy $a$ axis at 2 K shows
a very rapid increase caused by a small field—the magnetic moment is practically saturated at
2 kOe. From the value of magnetization at $H = 80$ kOe, the lower limit for the average Co
moment was found to be 3.6 $\mu_B$. From the inset of this figure, it is evident that there is no
significant remanent magnetization in zero field (less than 4% of the saturation magnetization)
and no significant hysteresis, within the measurement field resolution of 50 Oe. From the
neutron diffraction data [7] it has been seen that in the ferromagnetic state the system is not
completely ordered; the magnetic moment on one of the two Co sites only has a value of
approximately 1.81(4) $\mu_B$. In order to fully understand this magnetization process, one should
take into consideration not just the trivial movement of domain walls but also the possible
elongation of existing magnetic moments in an applied magnetic field.

In the antiferromagnetic phase at 8 K, it is again very easy to saturate the magnetization. In
the small field range before saturation, the system clearly passes through a region of hysteresis
centred around 2.7 kOe indicating the presence of an additional phase transition. The phase
transitions are also clearly seen as anomalies in the $\chi(T)$ curves at low fields. However, by
6 kOe, the susceptibility curve is very smooth, making it impossible to pin-point the transition
temperature. Specific heat measurements may prove more useful for plotting the phase diagram
for $H \parallel a$, as has been demonstrated for the Ni$_3$V$_2$O$_8$ phase diagram [3].
Figure 1. Left panel: characteristic magnetization curves for each of the three main crystallographic directions of $\text{Co}_3\text{V}_2\text{O}_8$. The 2 K data lie within the ferromagnetic phase, and the 8 K data in the antiferromagnetic phase. For $H \parallel a$, the inset of the top panel shows there to be no significant hysteresis around zero field in the ferromagnetic phase (within the 50 Oe field resolution of our measurements) and a considerable hysteresis observed around 2.7 kOe in the antiferromagnetic phase. For $H \parallel c$, the derivatives of magnetization, $dM/dH$, indicate more definitely the location of phase transition fields, as can be seen in the inset on the bottom panel. Right panel: characteristic susceptibility curves for each of the three main crystallographic directions performed with various applied fields. The black arrows indicate the locations of the paramagnetic to antiferromagnetic or antiferromagnetic to ferromagnetic phase transitions. The grey arrow points to the feature in the $\chi(T)$ curve associated with the locking of the incommensurate antiferromagnetic structure into a particular value of the magnetic propagation vector (see main text for details).

(This figure is in colour only in the electronic version)
From the magnetization curves shown for $H \parallel b$, it is obvious that the (010) direction is the hard axis of the system. In a field of 80 kOe, the average magnetic moment is less than 40% of that found for a field applied along the $a$ axis. The $\chi(T)$ curves measured for these two directions differ by a factor of almost 100 \cite{9}. In the ferromagnetic phase at 2 K, the $M(H)$ curve shows two step-like hysteretic anomalies at 58 and 64 kOe. These features, and others, are easily followed across $\chi(T)$ curves measured in different applied fields. From comparison with neutron powder diffraction data it is obvious that the anomaly observed at around 11 K corresponds to the transition from a paramagnetic state to an antiferromagnetic state. The neutron data also show that the feature at around 6 K corresponds to the transition from an antiferromagnetic state to a ferromagnetic state. These two transitions are shown by black arrows on the $\chi(T)$ curve measured at 60 kOe. The grey arrow corresponds to an anomaly associated with the unlocking of the propagation vector from $(0, 0.5, 0)$ within the antiferromagnetic phase.

For $H \parallel c$ in the ferromagnetic phase at 2 K, the saturation magnetic moment approaches that for $H \parallel a$. The $M(H)$ curve for $H \parallel c$ shows multiple features at 9.5, 46 and 51 kOe. To

\footnote{Reference \cite{9} uses a different notation to this paper and to reference \cite{6} for labelling axes; space group $A2/ac$ was used, so the $c$ and $a$ axes are swapped.}
observe all of these, the derivative of the magnetization must be considered. These irregularities can also be followed in the $\chi(T)$ curves.

All features observed in the $\chi(T)$ and $M(H)$ curves for $H \parallel b$ and $H \parallel c$ are summarized in the magnetic phase diagram in figure 2. The reduced symmetry and large number of competing interactions in the system contribute to the complex nature of this diagram. It comprises a high temperature paramagnetic phase, an intermediate antiferromagnetic phase and a low temperature ferromagnetic phase. These phases evolve differently as the temperature is reduced and the field increased along different directions. There is added complexity from the anomalies associated with the locking and unlocking of the magnetic propagation vector.

The ordering temperature decreases significantly with applied magnetic field, for $H \parallel c$ for example, $T_N(40 \text{ kOe}) \approx 1/2 T_N(1 \text{ kOe})$. Such a dramatic decrease in the ordering temperature is unusual even for highly frustrated systems.

A similar range of measurements has been performed on Ni$_3$V$_2$O$_8$, confirming the phase diagram reported by Lawes et al [3]. The diagram indicates that five phases exist at low temperatures: paramagnetic, high temperature incommensurate, low temperature incommensurate, and two commensurate phases. Along the $b$ and $c$ axes, the low temperature incommensurate phase is entirely enclosed by 80 and 30 kOe respectively, but open along the $a$ axis. Here, figure 3 (left panel) shows the phase diagram for an applied field parallel to the $a$ axis with an extension in magnetic field, up to 120 kOe. The $M(H)$ curves collected between 1.5 and 6 K show slight hysteresis at approximately 90 kOe (figure 3 right panel). This is evidence for the closing of the low temperature incommensurate phase not previously reported. In addition to the closing of this phase, the phase diagram here also contains a further phase boundary at around 20 kOe at the lowest temperature. This transition is evident from the large hysteresis observed in the $M(H)$ curves measured below 2 K.

4. Conclusions

The magnetization measurements performed on the Kagomé staircase compound Co$_3$V$_2$O$_8$ show there to be no significant net magnetization in zero field or hysteresis in the
low temperature ferromagnetic phase. The transitions from a paramagnetic state to an antiferromagnetic phase, and then to a ferromagnetic phase, are followed in temperature and applied field. The magnetic phase diagram, shown here for the first time, is complicated further by anomalies caused by the locking and unlocking of the propagation vector within the antiferromagnetic phase. The magnetic phase diagram of the closely related compound Ni$_3$V$_2$O$_8$ has been extended in magnetic field to show a new boundary that closes the low temperature incommensurate phase when the magnetic field is applied along the $a$ axis.

Acknowledgements

We are grateful to L C Chapon and B Fåk for discussion, to M R Lees for reading the manuscript, and to the EPSRC for financial support.

References

[1] Rogado N et al 2002 Solid State Commun. 124 229
[2] Rogado N et al 2003 J. Phys.: Condens. Matter 15 907
[3] Lawes G et al 2004 Phys. Rev. Lett. 93 247201
[4] Kenzelmann M et al 2006 Phys. Rev. B 74 014429
[5] Lawes G et al 2005 Phys. Rev. Lett. 95 087205
[6] Szymczak R et al 2006 Phys. Rev. B 73 094425
[7] Wilson N R, Petrenko O A and Chapon L C 2006 in preparation
[8] Sauerbrei E E, Faggiani R and Calvo C 1973 Acta Crystallogr. B 29 2304
[9] Balakrishanan G et al 2004 J. Phys.: Condens. Matter 16 L347