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Magnetic anisotropy in geometrically frustrated kagome staircase lattices

R. Szymczak [a], P. Aleshkevych [a], C.P. Adams [b,d], S.N. Barilo [c], A.J. Berlinsky [b,e], J.P. Clancy [b], V. Domuchowski [a], J. Fink-Finowicki [a], B.D. Gaulin [b,e], M. Ramazanoglu [b], S.V. Shiryaev [c], Z. Yamani [f], H. Szymczak [a,*]

[a] Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland
[b] Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, Canada
[c] Institute of Solid State and Semiconductor Physics, NAS, Minsk, Belarus
[d] Department of Physics, St. Francis Xavier University, Antigonish, Nova Scotia, Canada
[e] Canadian Institute for Advanced Research, Toronto, Ontario, Canada
[f] Canadian Neutron Beam Centre, NRC, Chalk River, Ontario, Canada

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ABSTRACT

This paper reviews experimental results concerning magnetic anisotropy in geometrically frustrated kagome staircase lattices. Following problems are discussed: high-temperature susceptibility measurements of kagome single crystals; inelastic neutron scattering measurements on $Co_3V_2O_8$ single crystals; EPR of Co^{2+} ions in kagome staircase $Mg_3V_2O_8$ single crystals. The single-ion anisotropy Hamiltonian is used to analyze experimental results. It is suggested that the magnetic anisotropy in kagome staircase $M_3V_2O_8$ (M = Co, Ni, Mn) oxides has mainly single-ion origin.

1. Introduction

Frustrated magnetic materials have recently attracted much interest, both theoretically and experimentally. This interest is stimulated by attempts to find new fundamental effects such as the magnetization plateaus and the magnetization jumps which represent a genuine macroscopic quantum effect. Of particular interest has been magnetism of the two-dimensional kagome staircase $M_3V_2O_8$ (M = Ni, Co, Mn) because of the concurrent presence of both highly frustrated lattice and strong quantum fluctuations. This system displays a rich, highly anisotropic, phase diagram [1–17]. Even though these materials have identical crystal symmetry and similar structural parameters, their magnetic properties are quite different. The difference between them may, in part, be attributed to the magnetocrystalline anisotropy, which is determined by electronic structure of magnetic ions.

To gain insights into the magnetic interactions in kagome staircase $M_3V_2O_8$ oxides, we decided to investigate their magnetic anisotropy using various experimental methods.

2. Structural and magnetic properties

The crystal structure of kagome staircase $M_3V_2O_8$ oxides was found to be orthorhombic (space group Cmca). No structural phase transitions were detected from helium up to room temperature. The magnetic behavior of kagome staircase compounds may be described in terms of two nonequivalent magnetic ion sites, known as spine sites and cross-tie sites. The ordering in these materials involves spin component aligned along the *a*-direction. The magnetic structure always involves ordering of the spine spins. Magnetic susceptibility, neutron diffraction and specific heat measurements revealed that kagome staircase compounds undergo a cascade of magnetic phase transitions versus temperature and magnetic field. It is a consequence of the competing exchange interactions (nearest and next nearest-neighbor exchange) and the inherent frustration.

3. High-temperature magnetic susceptibility

The characteristics of magnetocrystalline anisotropy and crystal field parameters may be obtained from the high-

* Corresponding author. Tel.: +0 048 22 8436601; fax: +0 048 22 8430926.
E-mail address: szymh@ifpan.edu.pl (H. Szymczak).

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temperature magnetic susceptibility tensor, whose components are given asymptotically at high temperatures ($T \gg |\theta_i|$) as

$$\chi_{ii} = C_i/(T + \theta_i)$$

where i labels the Cartesian components in orthorhombic coordinate system. The experimental data will be analyzed using the Hamiltonian of the form

$$\hat{H} = \Sigma_i H^i_{cr} - 1/2\Sigma_{ij} I_{ij} J_i J_1 + \mu_B H \Sigma_i g_1 J_i$$

where

$$H^i_{cr} = \sum_{k,q} B_{kq} O^q_k$$

describes the crystal field potential; J is the angular momentum; I_{ij} is the exchange integral; μ_B is the Bohr magneton, $O_k{}^q$ are the Stevens operators.

Following Ref. [18], the Hamiltonian $\hat{H}$ may be considered in molecular field approximation what results in the following expressions for crystal field and molecular field parameters and their relation with magnetic susceptibility χ_{ii}:

$$\chi_{ii}^{-1} = 3T[g_i^2 \mu_B^2 J(J+1)(1 + \theta_i/T)^{-1} - \lambda$$

$$\lambda = \text{const}(\theta_x + \theta_y + \theta_z)$$

$$\xi B_{20} = (1/3)(2\theta_z - \theta_x - \theta_y)$$

$$\xi B_{22} = \theta_x - \theta_y \quad \xi = 1/5(2J-1)(2J+3)$$

λ is the molecular field parameter proportional to the exchange integral I_{ij}.

In order to determine the crystal field acting on magnetic ions we have performed magnetic susceptibility measurements on $Ni_{3-3x}Co_{3x}V_2O_8$ ($x = 0$ and 0.03) and $Co_{3-3x}Mg_{3x}V_2O_8$ ($x = 0$, 0.05 and 0.1) single crystals (see Fig. 1 as an example).

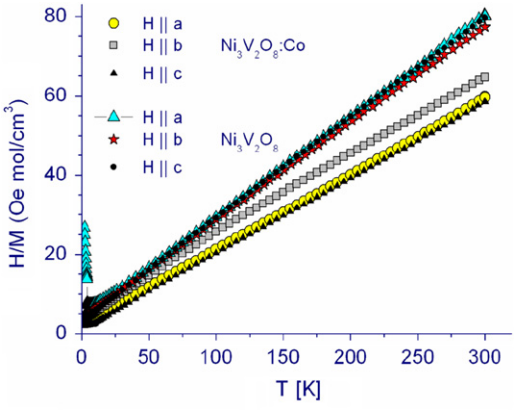

Fig. 1. χ^{-1}(T) for magnetic field applied along each of the crystallographic directions of $Ni_{3(1-x)}Co_{3x}V_2O_8$ ($x = 0$, 0.03).

A fit of the measured susceptibilities to the above equations yields the results gathered in Table 1. The above analysis is based on the assumption that spine sites and cross-tie sites are equivalent. This oversimplification, used also in Ref. [7], means that results presented in the table have rather qualitative character.

It results from Table 1 that the crystal field is considerably weaker in $Ni_3V_2O_8$ than in $Co_3V_2O_8$ crystals. Cobalt doping increases considerably crystal field parameters in $Ni_3V_2O_8$ and induces an easy axis along c-direction in agreement with the experimental data presented in Ref. [12]. Spin-flop transition clearly seen in Fig. 2 confirms that the a-direction is an easy axis in pure $Ni_3V_2O_8$ crystals. Doping with Co ions changes this easy axis to c-direction (see spin-flop transition diffused due to chemical disorder in Fig. 3).

In contrast, doping with nonmagnetic Mg^{2+} ions decreases considerably crystal field parameters in doped $Co_3V_2O_8$ crystals. These results show that the a-axis is an easy axis for pure and Mg-doped $Co_3V_2O_8$ crystals at $T = 2$ K.

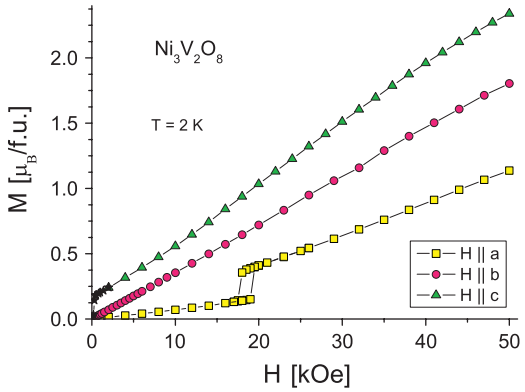

Fig. 2. Magnetization curves at 2 K for $Ni_3V_2O_8$.

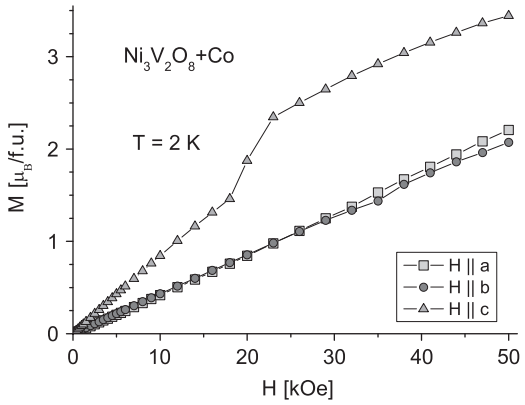

Fig. 3. Magnetization curves at 2 K for $Ni_3V_2O_8$:3% Co crystals.

Table 1
Paramagnetic Curie–Weiss temperatures and crystal field parameters for $Ni_{3-3x}Co_{3x}V_2O_8$ ($x = 0$ and 0.03) and $Co_{3-3x}Mg_{3x}V_2O_8$ ($x = 0$, 0.05 and 0.1).

Materials	NiV_2O_8 θ (K)	CoV_2O_8 θ (K)	NiV_2O_8 +3% Co θ (K)	CoV_2O_8 +5% Mg θ (K)	CoV_2O_8 +10% Mg θ (K)	$Ni_{2.45}Mn_{0.55}V_2O_8$ θ (K)
$H\|\|a$	15.8	−6.3	11.4	−4.9	−2.7	15
$H\|\|b$	17.6	114	31.1	99	86	15
$H\|\|c$	15.2	7.2	7.1	11.9	8.3	15
$\sum\theta_i$	48.4	114.9	49.6	106	91.6	45
B_{20}	−1.0	−13.0	−9.4	−9.8	−9.4	~0
B_{22}	−1.8	−50.1	−19.7	−43.3	−33.5	~0

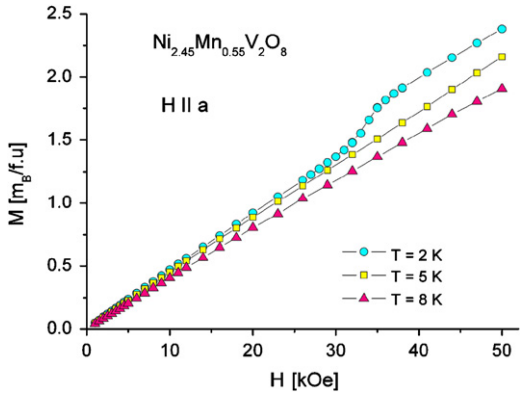

Fig. 4. Magnetization curves at 2 K for $Ni_{2.45}Mn_{0.55}V_2O_8$ crystals.

We have also studied $Ni_3V_2O_8$ single crystal heavy doped with Mn ions. The Mn^{2+} ions are the S-state ions and their contribution to the effective anisotropy is very low. The heavy doping does not change the easy axis direction of $Ni_3V_2O_8$ single crystal (see spin-flop transition in Fig. 4). As it was emphasized the results presented in Table 1 give the parameters of the total effective crystal field and not the separate contributions from nonequivalent spine sites and cross-tie sites. Nevertheless, the dependence of the crystal field parameters on the level of doping suggests that magnetic anisotropy in studied geometrically frustrated kagome staircase lattices has mainly single-ion character.

The only way to determine the separate contributions to magnetic anisotropy from nonequivalent spine sites and cross-tie sites is to use nuclear magnetic resonance (or Mössbauer spectroscopy) or inelastic neutron scattering techniques. Such measurements have been performed for the first time on $Co_3V_2O_8$ single crystals using inelastic neutron scattering technique [19]. The results yielded,

$$B_{20} = -5.8\,\mathrm{K}, \quad B_{22} = -13.9\,\mathrm{K}$$

for spine sites and

$$B_{20} = -8.2\,\mathrm{K}, \quad B_{22} = -27.8\,\mathrm{K}$$

for cross-tie sites.

Another (indirect) way to determine crystal field parameters acting on magnetic ions is to study the electron paramagnetic resonance (EPR) spectra of magnetically diluted kagome staircase compounds. We have performed such measurements for $Mg_3V_2O_8$ doped with 0.3% Co [20]. The EPR spectrum shows two groups of resonance lines associated with Co ions in spine sites and cross-tie sites. The position of experimental resonance lines can be described by a spin-Hamiltonian of orthorhombic symmetry:

$$\hat{H} = \mu_B(Hg\hat{S})$$

where the g-tensor was determined to be:

$$g_x = 2.42, \quad g_y = 3.36, \quad g_z = 7.04 \quad \text{for spine sites}$$

$$g_x = 3.47, \quad g_y = 6.1, \quad g_z = 3.25 \quad \text{for cross-tie sites.}$$

Taking into account that according to Ref. [19] the magnetic coupling between the spine and cross-tie Co ions $J = 1.25$ meV and the spine–spine coupling vanishes one may calculate the corresponding values of B_{20} and B_{22}. This gives:

$$B_{20} = 10.8\,\mathrm{K}, \quad B_{22} = -7.4\,\mathrm{K} \quad \text{for spine sites}$$

$$B_{20} = -0.6\,\mathrm{K}, \quad B_{22} = -20.6\,\mathrm{K} \quad \text{for cross-tie sites.}$$

Although, the method presented has some well known limitations (see Refs. [20,21]) nevertheless, the results obtained confirm significant contribution of single-ion mechanism to the effective magnetic anisotropy in $Co_3V_2O_8$ single crystals.

4. Conclusions

Various experimental methods have been used to determine magnetocrystalline anisotropy in geometrically frustrated kagome staircase oxides. It was shown that this anisotropy has mainly single-ion origin.

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