High Temperature Thermodynamics of the Multiferroic $Ni_3V_2O_8$

J. Oitmaa[a] and A. Brooks Harris[b]

[a] *School of Physics, The University of New South Wales, Sydney NSW 2052, Australia.*
[b]*Dept of Physics and Astronomy, University of Pennsylvania, Philadelphia PA 19104, U.S.A.*

We study a Heisenberg model proposed to describe the magnetic properties of the multiferroic material $Ni_3V_2O_8$. Using high-temperature expansions we compute the specific heat and zero-field susceptibility as functions of temperature. This will allow a comparison with experimental measurements.

1. Introduction

The nickel vanadate $Ni_3V_2O_8$ is a much studied material [1], with transitions at temperatures of 9.1K, 6.3K, 3.9K between various magnetically ordered phases, including a 'multiferroic' phase which shows simultaneous ferroelectric and magnetic order. The material itself is rather complex, with 6 magnetic Ni^{++} S=1 ions per orthorhombic unit cell, forming a structure of coupled 'Kagome staircase' planes, shown in Fig. 1.

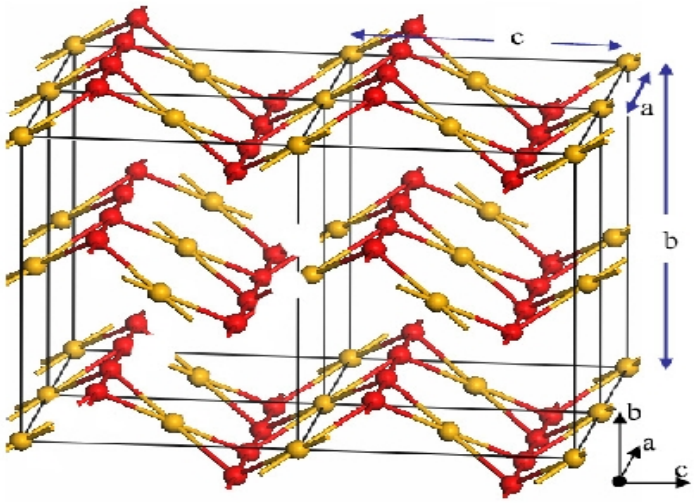

Fig. 1. Magnetic sites in $Ni_3V_2O_8$ showing the two types of Ni sites: 'spine' sites (dark circles) and 'cross-tie' sites (light circles). Figure reproduced from [1] with permission from IOP Publishing Copyright 2008.

An important feature of the magnetic interactions in this material is frustration, which is responsible for the complex sequence of ordered phases. The highest temperature ordered phase is incommensurate with the lattice, with moments predominantly on the spine sites. The ordering wavevector is largely determined by competition between nearest and next-nearest exchange interactions along the spines (J_1 and J_2 in Fig.2). The multiferroic phase sets in at a lower temperature 6.3K.

A first principles electronic structure calculation (LDA+U) [1] has identified as many as 12 different exchange constants, of which 5 appear to be dominant. These are shown as J_1, J_2, … J_5 in Figure 2. A set of proposed values (in meV), given in [1], is also shown. Of course, there is considerable uncertainty in these values.

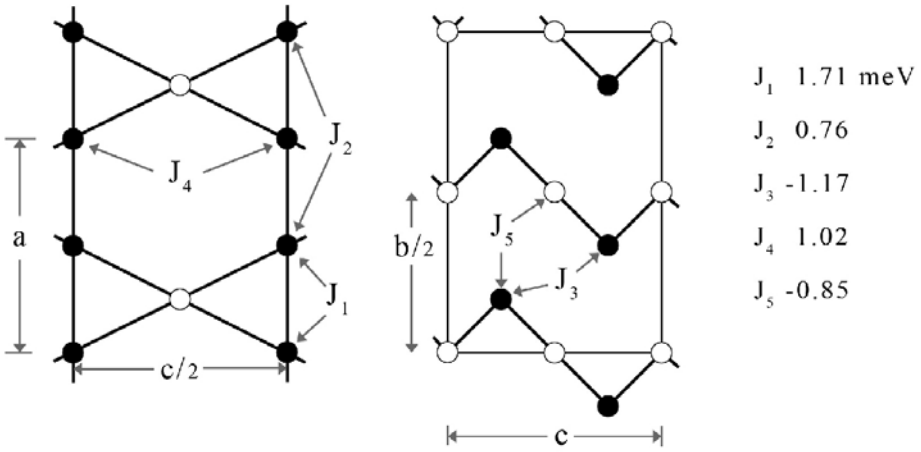

Fig.2. Dominant exchange interactions in $Ni_3V_2O_8$, and estimated values

The aim of the present work is to use a 5-parameter Heisenberg model and to calculate the specific heat and magnetic susceptibility in the paramagnetic phase, using high-temperature series expansions, and to compare with experimental data [2].

2. The calculation

We assume an isotropic Heisenberg model

$$H = \sum_{<ij>} J_{ij}\, \mathbf{S}_i \cdot \mathbf{S}_j - g\mu_B B \sum_i S_i^z$$

where the S_i are spin-1 operators, the first summation is over all exchange coupled pairs, with J_{ij} one of the five possible exchange parameters, and the final term is the interaction with an external magnetic field B. We derive high temperature expansions for the model by a standard linked-cluster method [3]. This approach has a long history, going back to the 1950's. However, we know of no previous such work with so many different exchange constants.

The expansions for the logarithm of the partition function Z per site, and for the zero-field susceptibility, take the form

$$\ln Z/N = \ln 3 + \sum_r a_r \beta^r$$

$$k_B T\chi / (g\mu_B)^2 = 2/3 + \sum_r c_r \beta^r$$

where $\beta = 1/k_B T$ is the expansion variable and the a_r, c_r are numerical coefficients whose values depend on the J's. The first few coefficients are, explicitly

$$a_2 = 4\,(J_1^2 + J_2^2 + J_3^2 + J_4^2 + 2J_5^2) / 9$$

$$a_3 = 2\,(J_1^3 + J_2^3 + J_3^3 + J_4^3 + 2J_5^3 - 8J_1^2 J_2 - 8J_1 J_5^2) / 27$$

$$c_1 = -16\,(J_1 + J_2 + J_3 + J_4 + 2J_5) / 27$$

$$c_2 = 20\,(J_1^2 + J_2^2 + J_3^2 + J_4^2) / 81 + 104 J_5^2 / 81 + 128\,(J_1 J_2 + J_1 J_3 + \ldots + J_4 J_5) / 81$$

We have carried out the calculation through 10^{th} order for the zero-field free energy and through 7^{th} order for the susceptibility. This involves 72577 and 364916 distinct clusters with five possible bond types, which are embeddable on the $Ni_3V_2O_8$ lattice. The resulting series can then be analysed by standard Padé approximant methods.

3. Results

In Table 1 we show the coefficients of the specific heat and susceptibility series for the particular J values given in Fig. 2.

Table 1. Series Coefficients for Specific Heat and Susceptibility

N	C/k_B	χ
0	$0.653866666667 \times 10^{1}$	$0.666666666667 \times 10^{0}$
1	$-0.106630202444 \times 10^{2}$	$-0.367407400740 \times 10^{0}$
2	$0.938305051214 \times 10^{0}$	$-0.114674567901 \times 10^{1}$
3	$-0.407665087950 \times 10^{2}$	$0.503738067490 \times 10^{1}$
4	$0.480120021243 \times 10^{3}$	$-0.143967012941 \times 10^{2}$
5	$-0.228030693775 \times 10^{4}$	$0.375923499903 \times 10^{2}$
6	$0.861441411583 \times 10^{4}$	$-0.845223517854 \times 10^{2}$
7	$-0.342195552001 \times 10^{5}$	$0.173902466284 \times 10^{3}$
8	$0.147719535268 \times 10^{6}$	

As is apparent, the series terms alternate in sign. This indicates a dominant singularity on the negative β axis, and makes the analysis somewhat problematic. Indeed, it is not possible to determine the position of the critical point with any accuracy. However at higher temperatures (smaller β) both quantities can be evaluated from Padé approximants, with a fair degree of precision. The results are shown in Fig. 3.

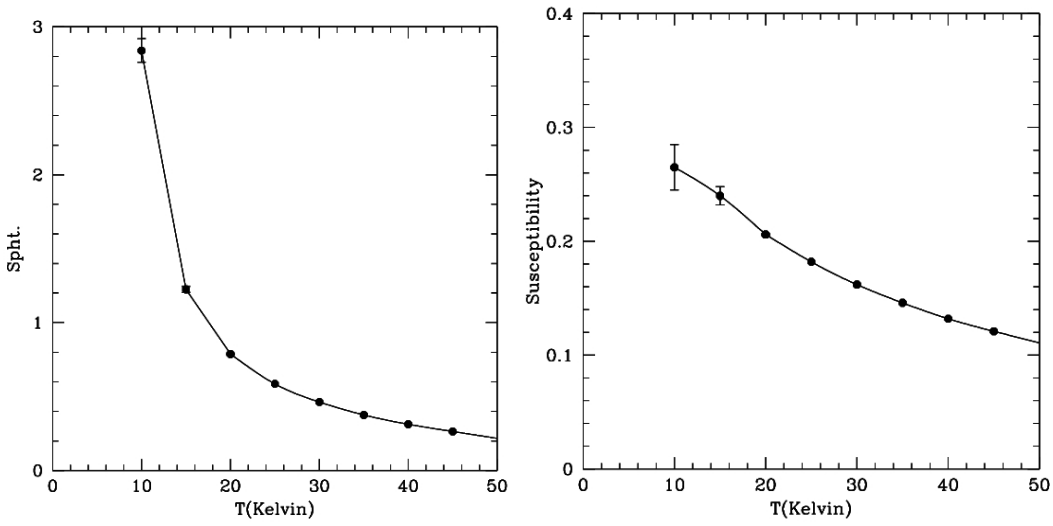

Fig.3. Specific heat and susceptibility for $Ni_3V_2O_8$ versus temperature, obtained from the 5-parameter Heisenberg model. The data points are averages of high-order Padé approximants, and the error bars indicate confidence limits, based on the degree of consistency between different approximants.

4. Discussion

We have computed the high-temperature specific heat and magnetic susceptibility of a 5-parameter Heisenberg model, believed to apply to the multiferroic material $Ni_3V_2O_8$. The specific heat shows evidence of a divergence around 10K, in good agreement with the actual transition temperature of 9.1K in $Ni_3V_2O_8$. We are not able to estimate the transition temperature of the model directly, as the specific heat series is not well suited to this. To make such an estimate would require a calculation of the magnetic structure factor. Our goal remains to compare our results in detail with the experimental data, and to attempt to constrain the values of the exchange parameters. This remains work in progress.

Our approach is applicable to the high temperature paramagnetic phase, and is able to probe the highest temperature transition, but is, of course, unable to probe the lower temperature transitions or ordered phases. This is, theoretically, a very difficult problem. An isostructural material $Co_3V_2O_8$ also shows interesting magnetic properties, and a similar study could be undertaken for that case.

Acknowledgments

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References

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