Phase diagrams of pseudo one-dimensional Heisenberg systems

Citation for published version (APA):

DOI:
10.1103/PhysRevLett.40.1108

Document status and date:
Published: 01/01/1978

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
Phase Diagrams of Pseudo One-Dimensional Heisenberg Systems

J. P. A. M. Hijmans, K. Kopinda, F. Boersma, and W. J. M. de Jonge

Department of Physics, Eindhoven University of Technology, Eindhoven, The Netherlands

(Received 13 January 1978)

We present the first theoretical results on the anomalous field dependence of the Néel temperature for a system of loosely coupled classical Heisenberg chains with orthorhombic anisotropy for different directions of the applied magnetic field. The results compare favorably with the experimental phase diagrams of a series of selected S = 1/2 compounds with varying degrees of one dimensionality and anisotropy.

The ordering temperature \( T_N(H) \) of a pseudo one-dimensional Heisenberg antiferromagnet may increase drastically when an external magnetic field is applied. This initially surprising effect has been documented recently by a number of experimental results.\(^1\)\(^5\) It seems that the theoretical approach suggested by Villain and Loveluck,\(^6\) which is based on the behavior of the correlation length within the individual chains in the classical spin model,\(^7\)\(^\text{10}\) gives at least the right order of magnitude. However, as we will show, the drastic influence of some anisotropy resulting in essentially different phase boundaries with the field applied along different directions (including the introduction of a spin-flop phase) cannot be reproduced by this isotropic theory. Therefore a conclusion about the validity of the description of this effect is precluded so far.

In this Letter we will present the first results of a transfer-matrix approach for the classical Heisenberg chain with small orthorhombic anisotropy. We will show that this approach is capable of reproducing the field dependence of the Néel temperature in a series of real pseudo one-dimensional Heisenberg S = 1/2 systems with the field along each of the three principal axes.

In Figs. 1–3 our data on the phase diagrams are presented for a selected, representative series of pseudo one-dimensional systems. Some characteristic parameter values of this series are tabulated in Table I. The data were obtained from a continuous heating method, thus identifying the transitions by the maxima in the specific heat. From inspection of these results it is obvious that in a general sense the rise in \( T_N(H) \) strongly depends on the degree of one dimensionality, characterized by the entities in Table I. This indicates that basically the understanding of this anomalous behavior must be sought in the properties of the individual chains. Therefore, we will treat the system as consisting of loosely coupled chains.

For such a system \( T_N \) is implicitly given in the mean-field approach by

\[
2\pi d' \chi(T_N(H), H) = 1,
\]

\( d' = 1, \) is the parameter of the mean-field approach.

\( \chi \) is the magnetic susceptibility, and \( T_N(H) \) is the Néel temperature.

FIG. 1. Experimental phase diagram of (NC\(_5\)H\(_5\))\(_2\)MnCl\(_3\)·H\(_2\)O (PMC), together with the theoretical predictions. Data for the hard axis are not shown since they reveal a more complicated phase diagram which is most likely due to a small canting of the magnetic moments.

\( d' \) is the parameter of the mean-field approach.

\( \chi \) is the magnetic susceptibility, and \( T_N(H) \) is the Néel temperature.

\( d' = 1, \) is the parameter of the mean-field approach.

\( \chi \) is the magnetic susceptibility, and \( T_N(H) \) is the Néel temperature.

\( d' \) is the parameter of the mean-field approach.

\( \chi \) is the magnetic susceptibility, and \( T_N(H) \) is the Néel temperature.

\( d' \) is the parameter of the mean-field approach.

\( \chi \) is the magnetic susceptibility, and \( T_N(H) \) is the Néel temperature.
where \( \chi \) is the staggered susceptibility of an isolated chain and \( J' \) is interchain interaction. Hence we will have to evaluate the staggered susceptibility, \( \chi(T, H) \), of an isolated chain with orthorhombic anisotropy. We will not apply the usual approximation of \( \chi \) in terms of the correlation length.\(^6\)\(^{16} \) As we are dealing with high-spin (\( S = \frac{3}{2} \)) systems we will evaluate \( \chi \) in the framework of the classical spin model. Moreover, it has previously been shown that the classical model gives remarkably good results for those thermodynamic variables in the paramagnetic state which greatly depend on long-range correlation.\(^7\)\(^{18} \)

We will consider here the classical nearest-neighbor Hamiltonian of orthorhombic symmetry,

<table>
<thead>
<tr>
<th>Compound</th>
<th>( T_N(0) ) (K)</th>
<th>( J/k ) (K)</th>
<th>( S_{\text{crit}} )</th>
<th>( J'/J )</th>
<th>( \alpha )</th>
<th>( \beta/\alpha )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NC(_2)H(_5))MnCl(_3) H(_2)O</td>
<td>2.38</td>
<td>-0.7</td>
<td>39%</td>
<td>7 \times 10(^{-2} )</td>
<td>4 \times 10(^{-2} )</td>
<td>1.5</td>
<td>11</td>
</tr>
<tr>
<td>CsMnBr(_3) 2H(_2)O</td>
<td>5.76</td>
<td>-2.6</td>
<td>15%</td>
<td>10(^{-2} )</td>
<td>1 \times 10(^{-2} )</td>
<td>3</td>
<td>12, 13</td>
</tr>
<tr>
<td>CsMnCl(_3) 2H(_2)O</td>
<td>4.89</td>
<td>-3.0</td>
<td>12%</td>
<td>8 \times 10(^{-3} )</td>
<td>4 \times 10(^{-3} )</td>
<td>4</td>
<td>13</td>
</tr>
<tr>
<td>(CH(_3))(_2)NH(_2)MnCl(_3)</td>
<td>3.60</td>
<td>-5.8</td>
<td>3%</td>
<td>10(^{-3} )</td>
<td>1.15 \times 10(^{-3} )</td>
<td>8</td>
<td>14</td>
</tr>
</tbody>
</table>

According to the above classical nearest-neighbor Hamiltonian, we expect the following phase transitions for the CsMnCl\(_3\) 2H\(_2\)O and CsMnBr\(_3\) 2H\(_2\)O compounds. Further work on these compounds is in progress.
given by
\[ 3c_{\text{chain}}(\mathbf{S}_i, \mathbf{S}_{i+1}) = \sum_{m=-\infty}^{\infty} \frac{1}{2} g_0 H S_i (S_i^z + S_{i+1}^z) + 2J S(S + 1) [\mathbf{S}_i \cdot \mathbf{S}_{i+1} + \delta(S_i^x S_{i+1}^x - \frac{1}{2} \mathbf{S}_i \cdot \mathbf{S}_{i+1}) + \epsilon(S_i^y S_{i+1}^y - S_i^z S_{i+1}^z)], \]
(2)

where
\[ S_i = (S_i^x, S_i^y, S_i^z) = (\cos \varphi_i \sin \theta_i, \sin \varphi_i \sin \theta_i, \cos \theta_i). \]
(3)

The central problem in the transfer-matrix approach is to solve the integral equation
\[ \int_0^\pi d\theta_2 \int_0^{2\pi} d\varphi_2 \sin \theta_2 \exp[-3(\mathbf{S}_i, \mathbf{S}_2)/kT] \psi(\theta_2, \varphi_2) = \lambda \psi(\theta_1, \varphi_1) \]
(4)

because all static properties of the chain can be formulated in terms of the eigenvalues and eigenfunctions of this equation.

In order to reduce the number of integration variables in Eq. (4) we introduce the Fourier expansions
\[ \psi(\theta_1, \varphi_1) = (2\pi \sin \theta_1)^{-1/2} \sum_{m=-\infty}^{\infty} \Phi_m(\theta_1) \exp(i m \varphi_1) \]
(5)

and
\[ \exp[-3(\mathbf{S}_i, \mathbf{S}_2)/kT] = (2\pi)^{-1} \sum_{m=-\infty}^{\infty} \sum_{j=-\infty}^{\infty} K_{m,j}(\theta_1, \theta_2) \exp(i(m \varphi_1 - k \varphi_2)). \]
(6)

Substitution of Eqs. (5) and (6) in Eq. (4) yields [because of the orthogonality of the functions \( \exp(i m \varphi_1) \)] the set of coupled integral equations
\[ \sum_{j=-\infty}^{\infty} \int_0^\pi d\theta_2 \exp(i m \varphi_2) \Phi_{m,j}(\theta_1, \theta_2) = \lambda \Phi_m(\theta_1), \quad m = 0, \pm 1, \pm 2, \ldots. \]
(7)

It will be clear that Eq. (7) cannot be handled numerically unless the infinite summation is truncated in some way. In the case of axial symmetry around the field direction\(^6\) the truncation is possible because one finds a rapid decrease in magnitude of the \( K_{m,j}(\theta_1, \theta_2) \) with increasing \( |m - j| \). Moreover, only a restricted number of equations has to be retained because the susceptibilities depend mainly on the perturbed eigenstates related to \( m = 0, \pm 1 \) in the axially symmetric case. Even after this truncation, practical calculations are almost impossible without further simplifications. However, exploiting the \( C_2 \) symmetry of the system, Eq. (7) can be factorized into four smaller subsets. The integrals over \( \theta_1 \) occurring in each of these subsets are approximated by a discrete quadrature scheme. The choice of a set of values for \( \theta_1 \) identical to the abscissas used in the integration over \( \theta_2 \) results in a matrix eigenvalue equation\(^8\) which can be diagonalized by standard routines. The dimension of these matrices, which ultimately sets a limit to the applicability of the method, increases progressively when \( |J|/kT \) increases because both the number of coupled equations and the number of abscissas needed to obtain results of sufficient accuracy grow rapidly at lower temperatures.

Using the method sketched above, we calculated phase diagrams for \((\text{NC}, \text{H}_2)\text{MnCl}_2 \cdot \text{H}_2\text{O}\) (PMC), \(\text{CsMnBr}_2 \cdot 2\text{H}_2\text{O}\) (CMB), \(\text{CsMnCl}_3 \cdot 2\text{H}_2\text{O}\) (CMC), and \((\text{CH}_3)\text{NH}_2\text{MnCl}_3\) (DMMC). In order to eliminate the interchain molecular-field constant \( zJ' \), Eq. (1) was applied in the form \( \chi(T_\phi(H), H) = \chi(T_\phi(0), 0) \), where \( \chi \) is the appropriate staggered susceptibility. Basically we did not use adjustable parameters; the values for \( J \) were fixed to the reported values. From the zero-field energy differences, per spin, between the antiferromagnetically aligned states parallel to the easy and intermediate axis (\( \Delta E_3 \) and the easy and hard axis (\( \Delta E_2 \)) we define the reduced anisotropy energies \( \alpha \) and \( \beta \) as
\[ \alpha = \Delta E_3/2 |J| S(S + 1), \quad \beta = \Delta E_2/2 |J| S(S + 1). \]
(8)

Note that the values of \( \epsilon \) and \( \delta \) for given \( \alpha \) and \( \beta \) depend upon the correspondence between the coordinate system \( x, y, z \) and the magnetic axes. For CMC and CMB, \( \alpha \) and \( \beta \) were taken from the literature,\(^12,13\) whereas for PMC and DMMC the anisotropy parameters were obtained in an analo-
gous way, as will be reported elsewhere.\textsuperscript{19} Theoretical phase diagrams obtained with quadratic single-ion anisotropy instead of Eq. (2) showed only minor deviations from the results presented in Figs. 1-3.

With the field applied along the easy axis, we have to consider two different susceptibilities corresponding to the directions of the staggered field in the antiferromagnetic and spin-flop state. The phase boundaries found in this way intersect at the bicritical field $H_{\text{bic}}$ which is given to a very good approximation by $g\mu_B H_{\text{bic}} = 4|J|S\sqrt{2}\alpha$. For fields higher than $H_{\text{bic}}$ the spin-flop phase yields the highest, and thus physically realized, value of $T_N(H)$, while for fields smaller than $H_{\text{bic}}$ the situation is reversed.

The agreement between experimental and theoretical results is satisfying but it deteriorates somewhat at higher values of the reduced field $g\mu_B H/2|J|S$. Whether this is due to a deficiency in the applicability of Eq. (1) at high fields remains to be seen. Possibly a self-consistent type of approach would give better results. However, these high-field deviations could also be due to the suppression of quantum fluctuations, as described by Imry, Pincus, and Scalapino.\textsuperscript{16} Therefore it seems worthwhile to investigate the effect of quantum corrections on the present theory. The results of the present analysis may be summarized by stating that the, at first sight, anomalous behavior of the phase boundaries of pseudo one-dimensional Heisenberg systems can be quantitatively understood from the behavior of the staggered susceptibilities of the isolated chains, provided that the orthorhombic anisotropy terms are not neglected.

The authors wish to acknowledge the assistance of J. C. Schouten, J. Millenaar, and J. A. M. Roos. This research is partially supported by the Stichting Fundamenteel Onderzoek der Materie.


15See, for instance, Y. Imry, Phys. Rev. B \textbf{13}, 3018 (1976), and references therein.


