Magnetic studies and critical behaviour in Zn₄Cd₁₋ₓCrₓSe₄ compounds (0.35 ≤ x ≤ 0.45)

M. Hamedoun*, A. Hourmatallah, N. Benzakour, F. Mahjoubi and M. Houssa

Laboratoire de Physique du Solide, Département de Physique, Faculté des Sciences Dhar Mahraz B.P. 1796 Atlas - Fès, Maroc.

Magnetization measurements were presented in this paper for the spinel solid solutions Zn₄Cd₁₋ₓCrₓSe₄ for x = 0.35, 0.41 and 0.45. The Cr moment is 2.8 μₜCr where the magnetization saturates for fields up to 10 kOe at low temperature. The ferromagnetic scaling properties permit to determine the critical temperature Tc and the critical exponents β, γ and δ. Whereas the compounds with x=0.35 and 0.41 exhibit exponents compatible with a 3D Heisenberg ferromagnetic model, a slight increase of β, γ and decrease of δ were found for x=0.45. The Kadanoff scaling law γ = β(δ - 1) is satisfied by the experimental data. Using the mean field theory and the spin-wave theory at low temperature, the exchange integrals were calculated up to the third nearest neighbours (tun).

PACS: 75 30K, 75 30E, 75 10J, 75 60E

I. INTRODUCTION

Solid solutions of thiospinel and selenospinel have received considerable attention for their interesting magnetic and electrical properties 1-3. 

In the solid solution Zn₄Cd₁₋ₓCrₓSe₄, where Zn and Cd ions occupy the tetragonal sites A while Cr ions occupy the octahedral sites B of a normal spinel lattice, the behaviour changes from semiconducting and ferromagnet for x = 0 to insulating and complex antiferromagnet 4 with a helical spin structure for x = 1. In an intermediate range of composition (0.45 < x < 0.49) a spin-glass-like behaviour has been observed 5.

The purpose of this paper is to study the properties derived from magnetic isotherms in the asymptotic critical region (T=Tc) for the concentration x = 0.35, 0.41 and 0.45. As was reported in 6 the two first compositions are situated in the ferromagnetic region while the last concentration shows spin-glass-like re-entrant behaviour.

In order to determine the critical temperature Tc, the critical exponents β for the spontaneous magnetization (M), γ for the susceptibility (χ) and δ for the magnetization at T = Tc, several curves representing the field (H) dependence of the magnetization are performed on the three compounds at different temperatures close to Tc.

It's shown that for x = 0.35 and 0.41 all intra-plane and inter-plane interactions are positive. Hence the systems order ferromagnetically. However, for x=0.45 the interaction between next-nearest neighbour planes is negative but the stability condition of the helimagnetic phase is not satisfied. The appearance of the re-entrant phase for x > 0.41 is due to the fact that the competition between the interactions is insufficient to lead to an ordered helimagnetic phase.

This work has been the subject of two publications 3.

II. EXPERIMENTAL

Zn₄Cd₁₋ₓCrₓSe₄ system with x = 0.35, 0.41 and 0.45 were prepared, at T = 800°C, in polycrystalline form in evacuated quartz tube. We start from a mixture of the selenides ZnSe, CdSe and CrₓSe₃. X-ray diffraction showed the samples to be composed of a single spinel phase in the whole concentration range. The lattice parameters varied with the composition x in accordance with Vegard's rule.

Magnetic measurements were performed with a vibrating simple magnetometer in the temperature range 4.2 - 300 K and a field up to 18 kOe. The sample temperature was controlled to within a stability of ±0.02 K. The relative error of the magnetization and field measurements was estimated to be less than 5%.

III. RESULTS

A. Determination of Tc by magnetic measurements and Arrott plot method

Figure 1 shows the field dependence of the magnetization for Zn₀.₃₅Cd₀.₆₅CrₓSe₄ at different temperatures. In order to evaluate the Cr moment, let us examine the results at 4.2 K.

![Fig. 1](image.png)

Fig. 1. The field dependence of the magnetization for Zn₀.₃₅Cd₀.₆₅CrₓSe₄ at different temperatures.

The magnetization begins to saturate for fields close to 10 kOe. For higher fields, a small susceptibility is seen. So, knowing the compound moment, the Cr moment can be calculated and it is found to be 2.8 μₜCr. This value is not very different from the theoretical value gμₜB where

* Corresponding author
$S = \frac{3}{2}$ is the chromium spin number.

The Curie temperature $T_c$ was obtained from the Arrot’s plots ($M^2$ versus $H/M$) and the results for $x = 0.35$ is shown in Fig. 2. The same procedure is used to determine $T_c$ for $x = 0.41$ and 0.45. The values found by this method are respectively ($T_c = 79, 72$ and 70 K) and different from those reported in Ref. 1 based on susceptibility measurements which are respectively ($T_c = 70, 62$ and 55 K). This difference arises from the difficulty in measuring $T_c$ which is caused by the presence of a short-range order of the spins above $T_c$. In order to illustrate this fact we report in Fig. 3 the dependence of the magnetization at field $H = 0.1$T for the three compounds studied: $x = 0.35, 0.41$ and 0.45. We see that the typical ferromagnetic behaviour is seen only at $T < T_c$. The curves do not drop at $T_c$ as may be expected for a pure ferromagnetic system but have only an inflexion point at $T_c$ and a smooth decrease for $T > T_c$. This effect is very clear as $x$ approaches the re-entrant domain. A supposition of a short-range ordering could explain this nonvanishing magnetization for $T > T_c$. In addition, the authors in Ref. 2 used magnetic measurements at relatively lower fields.

**B. Determination of $T_c$ and $\beta$, $\gamma$ and $\delta$ by the scaling plot method**

As an example, the measured magnetization $M$ as a function of the internal field $H_i$ ($H_i$ is the applied field corrected by the effects of demagnetization) at different temperatures is shown in Fig. 4 for $x = 0.45$.

It is well known that the second order phase transition around the temperature $T_c$ is characterised by a set of critical exponents $\beta$, $\gamma$ and $\delta$ defined in terms of the reduced temperature $t = \frac{T - T_c}{T_c}$ as follows: Just below $T_c$, the spontaneous magnetization is proportional to $t^{-\beta}$, just above $T_c$ the initial susceptibility is proportional to $t^{\gamma}$ and at $T = T_c$ the magnetization $M$ is proportional to $H_i^{-\delta}$.

The scaling plot is a useful method to study the phase transition in ordered and disordered systems. The static scaling law gives the following relation between the critical exponents: $\gamma = \beta (1 + \delta)$ and a magnetic equation of state given by:

$$\frac{M}{|t|^{\beta}} = f_{\pm}(\frac{H_i}{|t|^{\beta+\gamma}})$$

(1)

This equation implies that the reduced magnetization $m = \frac{M}{|t|^{\beta}}$ as a function of the reduced field $h_i = \frac{H_i}{|t|^{\beta+\gamma}}$ falls onto two different universal curves: $f_{\pm}(h_i)$ for temperatures below $T_c$ and $f_{\pm}(h_i)$ for temperatures above $T_c$.

**FIG. 2:** The Arrot plots for the compounds Zn$_{0.35}$Cd$_{0.65}$Cr$_2$Se$_4$ (The inset shows $M^2$ versus $T$).

**FIG. 3:** Temperature dependence of the magnetization at low field ($H = 0.1$T) for $x = 0.35, 0.41$ and 0.45. The arrows show the critical temperature $T_c$.

In practice, using a computer program, the transition temperature from the magnetic measurements was varied in a ±2 K range. The values of $\beta$ and $\gamma$ are first taken as those predicted for 3D Heisenberg ferromagnet. The plot of $\log(m)$ versus $\log(h_i)$ gives two families of curves with positive and negative curvatures. We then adjusted the values of the three parameters until we have a collapse of the isotherms onto two branches. Figure 5 shows a typical scaling plot for the composition $x = 0.45$. As can be seen, a good coincidence of the isotherms is obtained.

To determinate $\delta$, we have plotted $\log(h_i)$ versus $\log(M)$. The isotherm corresponding to the $T_c$ is a straight line.
From the slope of this line the exponent \( \delta \) was deduced, as shown in Fig. 6 for \( x = 0.45 \).

FIG. 4: Internal field dependence of the magnetization at various temperatures in the system \( \text{Zn}_{0.45}\text{Cd}_{0.55}\text{Cr}_2\text{Se}_4 \).

FIG. 5: Scaling plot of the magnetic isotherms in logarithmic form over the field range 0.1—18 kOe below and above Curie temperature for the \( \text{Zn}_{0.45}\text{Cd}_{0.55}\text{Cr}_2\text{Se}_4 \).

The critical temperature and the critical exponent values obtained for the three compositions are presented in Tab. 1. According to \(^{13}\) the scaling plot is relevant when considering data from a range equal to or smaller than the critical regime. This condition is respected in this study.

FIG. 6: Log-log plot of the magnetic isotherms for \( \text{Zn}_{0.45}\text{Cd}_{0.55}\text{Cr}_2\text{Se}_4 \) around and at \( T_c \). The dashed line corresponds to the adjusted power law.

IV. CALCULATION OF THE VALUES OF THE EXCHANGE INTEGRALS

The model used is the classical Heisenberg Hamiltonian:

\[
H = -2 \sum_{ij} J_{ij} S_i S_j
\]

(2)

where \( J_{ij} \) is the exchange integral between the spins situated at sites \( i \) and \( j \). The calculation are done under the supposition that exchange is different from zero only for an atom and its nn, nnn and tnn \( J_1 \), \( J_2 \) and \( J_3 \) respectively (Fig.7).

To determine the three exchange integrals we need three equations. The first is deduced from the Curie temperature \( T_c \). Holland and Brown \(^{14}\) have derived from mean field theory four possible expressions of \( T_c \) in the case of a normal cubic spinel lattice. They reported that the expression, most likely, which can describe the ferromagnetic portion of \( \text{Zn}_{0.45}\text{Cd}_{0.55}\text{Cr}_2\text{Se}_4 \) is:

\[
T_c = \frac{5}{2k_B} [2J_1 - 4J_2 - 4J_3]
\]

(3)

where \( k_B \) is the Boltzmann constant. (Contrary to ref. \(^{14}\) we consider the twelve exchange integrals between the tnn as identical).

The mean field theory gives also a second relation between the asymptotic Curie-Weiss temperature \( \theta_p \) and the exchange integrals \(^{15}\):

\[
\theta_p = \frac{5}{2k_B} [6J_1 + 12J_2 + 12J_3]
\]

(4)

The experimental values of \( \theta_p \) are taken from ref. \(^{16}\).

The third equation is derived from the spin-wave theory at low temperature. According to reference \(^{17}\), the plot of the magnetization \( M \) versus \( T \) shows very clearly that...
the Bloch’s law \( M(T) = M(0) [1 - B T^2] \) holds in a large range of temperature and the coefficient \( B \) is given for \( x = 0.35, 0.41 \) and 0.45.

\[
B = \frac{1.87 k_B}{QS \left( \frac{2S(J_1 + 10J_2 + 12J_3)}{J_1 + 10J_2 + 12J_3} \right)^{3/2}}
\]

where \( Q = 8 \) is the number of Cr atoms per unit cell.

In the treatment of spin-wave theory at low temperature the coefficient \( B \) in the equation of Bloch’s law is related to the exchange integrals \( J_1, J_2 \) and \( J_3 \) by the equation derived in the Appendix for the case of spinel lattice.

\[
I \left( \frac{48(J_2 + J_3)^2}{(J_1 + 10J_2 + 12J_3)^2} \right) = \frac{128(J_2 + J_3)^3}{(J_1 + 10J_2 + 12J_3)^3}
\]

Table 1. Critical temperature \( T_c (\pm 2 \text{K}) \), critical exponents \( \beta (\pm 0.04), \gamma (\pm 0.25), \delta (\pm 0.3) \) and reduced temperature range \( t \) used in ferromagnetic scaling plots for the system \( \text{Zn}_x\text{Cd}_{1-x}\text{Cr}_2\text{Se}_4 \) for \( x = 0.35, 0.41 \) and 0.45.

<table>
<thead>
<tr>
<th>( x )</th>
<th>( T_c (\text{K}) )</th>
<th>( \beta )</th>
<th>( \gamma )</th>
<th>( \delta )</th>
<th>( t ) range</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>66</td>
<td>0.40</td>
<td>1.50</td>
<td>4.85</td>
<td>-0.09 — 0.13</td>
</tr>
<tr>
<td>0.41</td>
<td>58</td>
<td>0.40</td>
<td>1.50</td>
<td>4.80</td>
<td>-0.1 — 0.15</td>
</tr>
<tr>
<td>0.45</td>
<td>52</td>
<td>0.42</td>
<td>1.55</td>
<td>4.70</td>
<td>-0.15 — 0.12</td>
</tr>
</tbody>
</table>

Table 2. Curie-Weiss temperature \( \theta_p \), Bloch’s coefficient \( B \) and values of the nn, nnn and tnn exchange integrals of \( \text{Zn}_x\text{Cd}_{1-x}\text{Cr}_2\text{Se}_4 \) as a function of the dilution \( x \).

<table>
<thead>
<tr>
<th>( x )</th>
<th>( \theta_p (\text{K}) )</th>
<th>( B (10^{-5} \text{K}^{-3/2}) )</th>
<th>( J_1/k_B (\text{K}) )</th>
<th>( J_2/k_B (\text{K}) )</th>
<th>( J_3/k_B (\text{K}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (^{18})</td>
<td>-</td>
<td>-</td>
<td>14</td>
<td>-0.10</td>
<td>-</td>
</tr>
<tr>
<td>0.35</td>
<td>172.80</td>
<td>63.30</td>
<td>12.36</td>
<td>-2.90</td>
<td>2.48</td>
</tr>
<tr>
<td>0.41</td>
<td>167.40</td>
<td>73.30</td>
<td>11.38</td>
<td>-0.91</td>
<td>0.80</td>
</tr>
<tr>
<td>0.45</td>
<td>163.80</td>
<td>76.70</td>
<td>10.66</td>
<td>0.36</td>
<td>-0.23</td>
</tr>
<tr>
<td>1 (^{19})</td>
<td>-</td>
<td>-</td>
<td>9.94</td>
<td>3.12</td>
<td>-4.26</td>
</tr>
</tbody>
</table>

Using equations (2), (3) and (4) we can determine \( J_1, J_2 \) and \( J_3 \). The optimum values are given in Table 2.

FIG. 7: Portion of spinel lattice showing the nn (B1), nnn (B2) and tnn (B3) of the magnetic ion B.

V. DISCUSSION

In diluted \( \text{Zn}_x\text{Cd}_{1-x}\text{Cr}_2\text{Se}_4 \) compounds, we have used the values of the critical temperature \( T_c \) derived from the scaling plot, the asymptotic Curie-Weiss temperatures \( \theta_p \) and the values of the constant \( B \) of Bloch’s law to determine the first three exchange integrals. We note that scaling permits to determine \( T_c \) that is very difficult to do from magnetization behaviour because cluster regime or short range order exists above \( T_c \).

The \( J_1 \) value is ferromagnetic and decreases when the A sites become more and more occupied by the Zn ions. It is situated between the values of the two extremely pure compounds \( \text{ZnCr}_2\text{Se}_4 \) and \( \text{CdCr}_2\text{Se}_4 \).

\( J_1 \) may be affected by a slight variation of the distance \( d_{Cr-Cr} \) between neighbouring chromium. This distance vary linearly with lattice parameter \( a \). This parameter is found to vary with the composition \( x \) in accordance with Vegard’s rule.

The long-range interactions Cr-Se-A-Se-Cr (A=Zn or Cd) would be expected to depend strongly on the A-site cation; indeed, the data on the Curie-Weiss temperature \( \theta_p \) of a large varieties of spinel shows a remarkable sensitivity to the nature of the A-site cation.

From the values of the \( J_1, J_2 \) and \( J_3 \) given in Table 2, we can derive the coupling between planes. For in-plane coupling, \( J_{aa} = 2J_1 + 4J_3 \). For interplane coupling, \( J_{ab} = 4J_1 + 8J_2 \). For coupling between nnn planes, \( J_{ac} = 4J_2 + 8J_3 \). For \( x = 0.35 \) and 0.41 all the inter and intraplane interactions are positive. Hence, the systems order ferromagnetically. For \( x = 0.45 \), the situation
different, a spin in a given plane is simultaneously
submissive to a strong ferromagnetic interaction $J_{ab}$ and a
weak antiferromagnetic one $J_{ac}$. It seems that this
competition is not sufficient to lead neither to a spin glass
state nor to a helical order. For the last case the condition
of stability $4|J_{ac}| > |J_{ab}|$ is not satisfied. For $x = 0$, the
parameters deduced from ref. 18 and presented in Table 2 are
estimated assuming all the more distant interactions to be
equally strong. However, the impressive analysis given by
Dwight and Menyuk 21 showed that the magnetic properties are
to a large extent the result of the errors bars with those for 3D
Heisenberg model, for a review, see 22. For the concentration
$x = 0.45$ the exponents deviate slowly from the values predicted
by this model and approach the values found in re-entrant systems.

Concerning the critical exponents $\beta, \delta, \alpha$ and $\gamma$ in the case
of the two concentrations $x = 0.35, 0.41$ their values are
consistent within the errors bars with those for 3D
Heisenberg model, for a review, see 22. For the concentration
$x = 0.45$ the exponents deviate slowly from the values predicted
by this model and approach the values found in re-entrant systems.

The values of $\delta$ determined directly from the plot of
$log(H_i)$ against $log(M)$ at $T = T_c$ are in good accordance
with those deduced from the Kadanoff scaling equation
$\gamma = \beta(\delta - 1)$. More detailed studies of the properties of the
spin-glass-like state will be presented elsewhere for $x > 0.45$ in the near future.

APPENDIX: FERROMAGNETIC SPIN WAVE THEORY IN THE SPINEL LATTICE

The spin-wave dispersion relation is given by:

$$E(k) = \frac{1}{N} \sum_{i,j} J_{ij} \exp(i k . R_{ij})$$

where $F(\mathbf{k}) = F(0) - F(k)$ is the Fourier
transform of the exchange integral. In a spinel lattice with the first three nn interactions ($J_1, J_2, J_3$) and for a long wave length, we obtain:

$$E(k) = \frac{a^2 S J_1}{8} [(k_x + k_y)^2 + (k_x - k_y)^2 + (k_x - k_z)^2]
+ \frac{a^2 S J_2}{8} [(2k_x + k_y - k_z)^2 + (2k_x - k_y + k_z)^2]
+ \frac{a^2 S J_3}{8} [(k_x - k_y)^2 + (k_x - k_z)^2 + (k_x + k_y)^2]
+ \frac{a^2 S J_2}{8} [(k_x + k_y - k_z)^2 + (2k_x + k_y + k_z)^2]
+ \frac{a^2 S J_3}{8} [(k_x - k_y)^2 + (k_x + k_y)^2 + (k_x - k_z)^2]
+ \frac{a^2 S J_2}{8} [(k_x - k_y)^2 + (k_x + k_y)^2 + (k_x - k_z)^2]
+ \frac{a^2 S J_3}{8} [(k_x - k_y)^2 + (k_x + k_y)^2 + (k_x - k_z)^2]$$

where $V$ is the Crystal volume, $M(T)$ is the magnetization
at temperature $T$. The integration is over all the $k$ space.

The volume $V = \frac{N a^3}{Q}$, where $N$ is the unit cell number
and $Q$ is the number of Cr atom per unit cell (in spinel case
$Q=8$). The zero temperature magnetization is
$M(0) = g \mu_B NS$. With these considerations, the expression (3A) leads to the Bloch's law:

$$M(T) = M(0) \left[ 1 - BT^{\frac{1}{2}} \right]$$

Where:

$$B = \frac{1.877}{QS} \left[ \frac{a^2 J_1 + 10J_2 + 12J_3}{25(S_1 + 10S_2 + 12S_3)} \right]^{3/2}$$

When $J_2 = J_3 = 0$ we obtain the formula given in ref. 17.

1. E. Agostinelli, C. Bahistoni, D. Fiorani, G. Mahogno and
   (1986).
3. M. Hamedoun, A. Zerhouni, A. Rachadi, M. Slimani and
4. M. Hamedoun, A. Hourmantallah, A. Zerhouni, N.
   Sol. (b) 203, 521 (1997).