Study of critical properties in B-spinel $Zn_xCd_{1-x}Cr_2Se_4$ ($0.35 \le x \le 0.58$)

N. Benzakour[a], M. Hamedoun[a]*, M. Houssa[a], A. Hourmatallah[a,b] and F. Mahjoubi[a].

a : Laboratoire de physique du solide. Département de physique, Faculté des Sciences Dhar Mahraz B.P, 1796 Atlas –Fès, Maroc.
b : Ecole Normale Supérieure B.P 5206 Fès Maroc.

The critical behaviour of the B-spinel $Zn_xCd_{1-x}Cr_2Se_4$ systems is studied in the concentration range $0.35 \le x \le 0.58$. The mean field theory and the ferromagnetic spin-wave theory at low temperatures are combined to calculate the exchange integrals up to the third nearest neighbours.

The ferromagnetic critical region is studied by the high-temperature series expansion (H.T.S.) extrapolated with the Padé (P.A) approximants method. The critical temperatures T_c and the critical exponents associated with the magnetic susceptibility (γ) and the correlation length (ν) are estimated. The obtained values of T_c are in good agreement with those obtained by magnetic measurements. The values of γ and ν are sensitive to the dilution ratio x. For the compounds situated in the ferromagnetic region ($0.35 \le x \le 0.41$), they are close to those of 3D Heisenberg model. For the compounds presenting re-entrant behaviour ($0.41 < x \le 0.58$), γ and ν deviate slowly from those of this model and approach the values found in re-entrant systems.

I. INTRODUCTION

Several investigations concerning the magnetic properties of the B-spinel $Zn_xCd_{1-x}Cr_2Se_4$ have been made[1-6]. The members of this family exhibit semiconducting and ferromagnetic behaviour for compounds rich on Cd ($0 \le x \le 0.41$) and insulating and complex antiferromagnetic behaviour for compounds rich on Zn ($0.58 < x \le 1$). In the intermediate range of concentration ($0.41 < x \le 0.58$), re-entrant properties are expected.

In a previous work[7], the interest was given to the critical behaviour of the system $Zn_xCd_{1-x}Cr_2Se_4$ in the concentration range ($0.35 < x \le 0.45$). In this paper we extend the investigations up to x = 0.58.

The experimental conditions and the preparation of the compounds have been described elsewhere[2,7].

Using the mean field theory and the ferromagnetic spin-wave theory at low temperature, the variation of the intra-plane and inter-plane interactions[8] with the ratio of dilution x is obtained in the range $0.35 \le x \le 0.58$. It is shown that for x=0.35 and x=0.41 all the inter-plane and intra-plane interactions are positive. Hence the systems order ferromagnetically. However, in the range $0.45 \le x \le 0.58$ the interaction between next nearest neighbour planes is negative but the stability condition[7] of the helimagnetic phase is not satisfied. The appearance of the re-entrant phase for $0.45 \le x \le 0.58$ is due to the fact that the competition between the interactions is insufficient to lead to an ordered helimagnetic phase.

The Padé approximant (P.A) analysis of the high-temperature series expansion (H.T.S.) of the correlation functions has been shown to be a useful method for the study of the critical region[9,10]. We have used this technique to determine the critical temperatures T_c and the critical exponents associated with the magnetic susceptibility and the correlation length γ and ν respectively. The series expansions for the susceptibility and the correlation length have been derived to the 6^{th} order in the reciprocal temperature for the B-spinel lattices including both nearest -neighbour and next-nearest-neighbour interaction in the Heisenberg model. Estimates of critical temperature T_c and critical exponents γ and ν for the system $Zn_xCd_{1-x}Cr_2Se_4$ are given in the range of concentration $0.35 \le x \le 0.58$. The obtained values of T_c are in good agreement with those obtained by the magnetic measurements. The variation of T_c with x is almost linear. The critical exponents are sensitive to the dilution ratio x.

The analysis of the data indicates that γ and ν are very sensitive to the consideration of the second neighbour exchange interaction.

II. CALCULATION OF THE VALUES OF THE EXCHANGE INTEGRALS

The model used is the classical zero-field Heisenberg hamiltonian :

$$H = -2 \sum_{i,j} J_{ij} S_i S_j \qquad (1)$$

where the J_{ij} is the exchange integral between the spins situated at sites i and j. The calculations are done under the assumption that exchange is different from zero only for nearest (nn), next nearest (nnn) and third nearest neighbours (tnn) with exchange integrals J_1, J_2 and J_3 respectively[7,8].

To determine the three exchange integrals we have used two relations derived directly from the mean field theory :

i) The relation between the asymptotic Curie-Weiss temperature θ_p and the exchanges integrals[11] :

$$\theta_p = \frac{5}{2k_B}\left[6J_1 + 12J_2 + 12J_3\right] \qquad (2)$$

where k_B is the Boltzmann constant.

The experimental values of θ_p are taken from[12].

ii) The relation between the Curie temperature T_c and J_1, J_2 and J_3 [13] :

$$T_c = \frac{5}{2k_B}\left[2J_1 - 4J_2 - 4J_3\right] \qquad (3)$$

The experimental values of T_c are estimated by the scaling plot method[2,7]. The variation of T_c with x is linear

* Corresponding author

and confirms the result of Baltzer[14] . We note that the predictions of the mean field theory are supported by quantitative agreement with the experimental result[15,16]

The third equation is derived from the spin-wave theory at low temperatures. In the whole range of concentration considered $0.35 \le x \le 0.58$, the plot of the magnetization M versus $T^{\frac{3}{2}}$ shows very clearly that the Bloch law $M(T) = M(0)[1 - BT^{\frac{3}{2}}]$ holds in a wide range of temperatures. In Figure 1, an example of magnetization curves for the compound x=0.58 measured in temperature range below T_c is presented. An example of the determination of the constant B from the slope of the curve $M(T)$ versus $T^{\frac{3}{2}}$ for x=0.58 is shown in Figure 2.

The obtained values for various concentration are given in Table 1. In the case of the B-spinel lattice, the coefficient B is related to J_1, J_2 and J_3 by[7] :

$$B = \frac{1.87}{QS}\left(\frac{k_B}{2S(J_1 + 10J_2 + 12J_3)}\right)^{\frac{3}{2}} \frac{1}{\left\{1 - \frac{48(J_2 + J_3)^2}{(J_1 + 10J_2 + 12J_3)^2} - \frac{128(J_2 + J_3)^3}{(J_1 + 10J_2 + 12J_3)^3}\right\}^{\frac{1}{2}}} \quad (4)$$

Where Q=8 is the number of Cr atoms per unit cell and $S = \frac{3}{2}$ is the spin number.

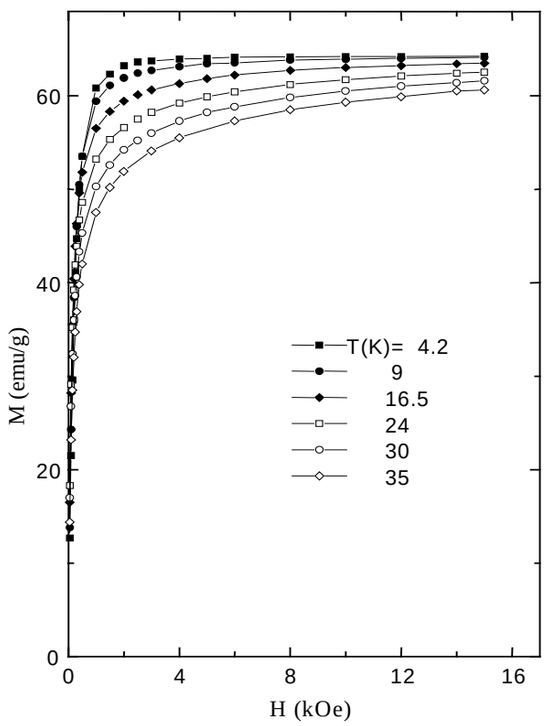

Figure 1 : Dependence of the magnetization M on the applied field H at various temperatures for $Zn_{0.58}Cd_{0.42}Cr_2Se_4$.

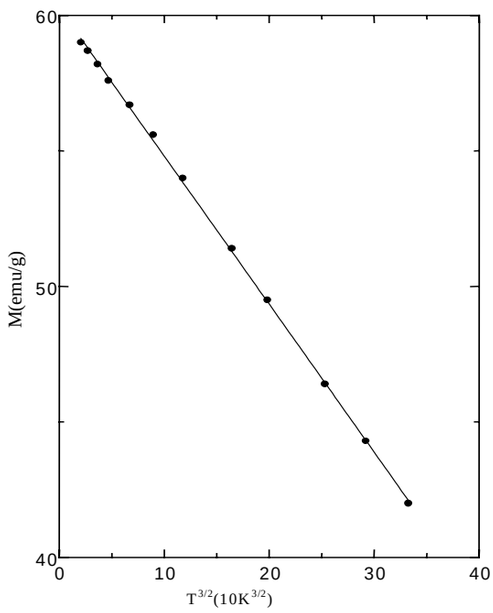

Figure 2 : $T^{\frac{3}{2}}$ dependence of magnetization in $Zn_{0.58}Cd_{0.42}Cr_2Se_4$ compound.

Using equations (2), (3) and (4) we have calculated J_1, J_2 and J_3. The optimum values are given in Table 1. In Figure 3, the variation of the intra-plane couplings, $J_{aa} = 2J_1 + 4J_3$ and the couplings between nearest, $J_{ab} = 4J_1 + 8J_2$ and next nearest plane, $J_{ac} = 4J_2 + 8J_3$ with x in the range $0.35 \le x \le 0.58$ are presented.

III. HIGH-TEMPERATURE SERIES EXPANSIONS

The uniform susceptibility per spin $\chi(T)$ may be expressed as :

$$\chi(T) = \frac{\beta}{N} \sum_{ij} \langle S_i S_j \qquad (5)$$

where $\beta = \frac{1}{k_B T}$, and $\langle S_i S_j = \frac{Tr S_i S_j e^{-\beta H}}{Tr e^{-\beta H}}$ is the correlation function between spins at sites i and j. The expansion of this function in power of β is obtained as follows[17]

$$\langle S_i S_j = \sum_{l=0}^{\infty} \frac{(-1)^l}{l!} \alpha_l \beta^l$$

In a recent work[18], the coefficients α_l required for the calculation of the three first correlation functions in the case of the B-spinel lattice are given. Here the H.T.S. are developed for $\chi(T)$ with arbitrary $\frac{J_2}{J_1}$ up to order 6. We obtain the following function :

$$\chi(T) = g\mu_B^2 \beta \sum_{m=0}^{n} \left(\sum_{n=1}^{6} a(m,n) y^m \tau^n \right) \qquad (6)$$

with $y = \frac{J_2}{J_1}$, $\tau = \frac{2S(S+1)J_1}{k_B T}$ and the coefficients $a(m,n)$ are presented in Table 2.

In ref.[18] , a relation between the correlation length and the three first correlation functions is given in the case of the B-spinel lattice with a particular ordering vector $Q = [0,0,k]$. In the ferromagnetic case we get k=0. The H.T.S. expansion of the $\xi^2(T)$ to order 6 in β gives the function

$$\xi^2(T) = \sum_{m=-n}^{n} \sum_{n=1}^{6} b(m,n) y^m \tau^n \qquad (7)$$

with the series coefficients $b(m,n)$ presented in Table 3.

x	T_c (K)	θ_p(K)	$B(10^{-5}\,K^{-3/2})$	$\frac{J_1}{k_B}$(K)	$\frac{J_2}{k_B}$(K)	$\frac{J_3}{k_B}$(K)	$\frac{\lvert J_{ac}\rvert}{4\lvert J_{ab}\rvert}$
0.35	66	172.80	63.3	12.36	-2.90	2.48	0.79
0.41	58	167.40	73.3	11.38	-0.91	0.80	3.46
0.45	52	163.80	76.70	10.66	0.36	-0.23	28.45
0.48	49	152	92.10	9.98	0.88	-0.69	5.87
0.55	41	145	103	9.03	1.68	-1.36	2.97
0.58	35	142	109	8.23	3.26	-2.64	1.82

Table 1 : Critical temperature Tc, Curie-Weiss temperature θ_p, Bloch's coefficient B, values of the nn, nnn and tnn exchange integrals and the ratio of the inter-plane interactions $\frac{\lvert J_{ac}\rvert}{4\lvert J_{ab}\rvert}$ of $Zn_xCd_{1-x}Cr_2Se_4$ as a function of dilution x.

(m,n)	a(m,n)	(m,n)	a(m,n)	(m,n)	a(m,n)	(m,n)	a(m,n)
(0,1)	2	(2,1)	0	(4,1)	0	(6,1)	0
(0, 2)	4	(2,2)	4	(4,2)	0	(6,2)	0
(0,3)	334/45	(2,3)	352/9	(4,3)	0	(6,3)	0
(0,4)	32/15	(2,4)	10364/135	(4,4)	3394/135	(6,4)	0
(0,5)	-472/4725	(2,5)	55008/675	(4,5)	135892/2025	(6,5)	0
(0,6)	5693/8505	(2,6)	208057/1890	(4,6)	3198569/8505	(6,6)	3633362/14175
(1,1)	4	(3,1)	0	(5,1)	0		
(1,2)	32/3	(3,2)	0	(5,2)	0		
(1,3)	272/9	(3,3)	196/15	(5,3)	0		
(1,4)	688/27	(3,4)	9652/135	(5,4)	0		
(1,5)	37972/2025	(3,5)	262274/2025	(5,5)	407441/28350		
(1,6)	1802051/85050	(3,6)	7402487/24300	(5,6)	3551491/5670		

Table 2 : Coefficients a(m,n) of the magnetic susceptibility : $\chi(T) = g\mu_B^2 \beta \sum_{m=0}^{n} \left(\sum_{n=1}^{6} a(m,n) y^m \tau^n \right)$

(m,n)	b(m,n)	(m,n)	b(m,n)	(m,n)	B(m,n)	(m,n)	b(m,n)
(-1,1)	1/384	(1,3)	71/960	(-5,5)	1/384	(-5,6)	25/288
(0,1)	1/96	(2,3)	-11/216	(-4,5)	11/576	(-4,6)	6971/3456
(1,1)	-1/32	(3,3)	-239/480	(-3,5)	199/19440	(-3,6)	1116229/77760
(-2,2)	-1/384	(-4,4)	-1/384	(-2,5)	-3541/10368	(-2,6)	131806583/3265920
(-1,2)	-5/288	(-3,4)	-1/54	(-1,5)	-8567939/5443200	(-1,6)	116427587/16329600
(0,2)	-53/576	(-2,4)	-1453/51840	(0,5)	-2377087/777600	(0,6)	-2984625341/1632960
(1,2)	-35/288	(-1,4)	61/540	(1,5)	-1555193/388800	(1,6)	-1816403531/8164800
(2,2)	1/9	(0,4)	7615/10368	(2,5)	-2377087/777600	(2,6)	1845120013/4082400
(-3,3)	1/384	(1,4)	16609/10368	(3,5)	128297/680400	(3,6)	3109320799/2332800
(-2,3)	31/1728	(2,4)	9701/8640	(4,5)	-259861/129600	(4,6)	335913673/259200
(-1,3)	397/8640	(3,4)	4831/5184	(5,5)	-7276231/1360800	(5,6)	261449537/453600
(0,3)	253/17280	(4,4)	21401/12960	(-6,6)	-1/384	(6,6)	429778829/4082400

Table 3 : Coefficients b(m,n) of the correlation length : $\xi^2(T)= \sum_{m=-n}^{n} \sum_{n=1}^{6} b(m,n) y^m \tau^n$

The simplest assumption that one can make concerning the nature of the singularity of the magnetic susceptibility $\chi(T)$ is that in the neighbourhood of the critical point the above two functions exhibit an asymptotic behaviour :

$$\chi(T) \propto (T_c - T)^{-\gamma} \quad (8)$$

$$\xi^2(T) \propto (T_c - T)^{-2\nu} \quad (9)$$

Estimates of T_c, γ and ν for $Zn_xCd_{1-x}Cr_2Se_4$ have been obtained using the P.A. method[19,20].

The [M,N] P.A. to the series $F(\beta)$ is a rational fraction $\frac{P_M}{Q_N}$, with P_M and Q_N, polynomials, of degree M and N in β, satisfying : $F(\beta) = \frac{P_M}{Q_N} + O(\beta^{M+N+1})$. The sequence of [M,N] P.A. to both the Log ($\chi(T)$) and Log($\xi^2(T)$) was found to be convergent. The simple pole corresponds to T_c and the residues to the critical exponents γ and ν. The obtained values of T_c, γ and ν are presented in Table 4.

IV. DISCUSSION AND CONCLUSION

In diluted $Zn_xCd_{1-x}Cr_2Se_4$ compounds the critical temperature *Tc* deduced from the scaling plot method, the asymptotic Curie-Weiss temperature θ_p and the constant *B* of the Bloch's law are used to determine the first three exchange integrals. From these values we have derived the variation of the intra-plane coupling, and the couplings between nearest, and next nearest plane, with x in the range of concentration $0.35 \le x \le 0.58$ (Figure 3).

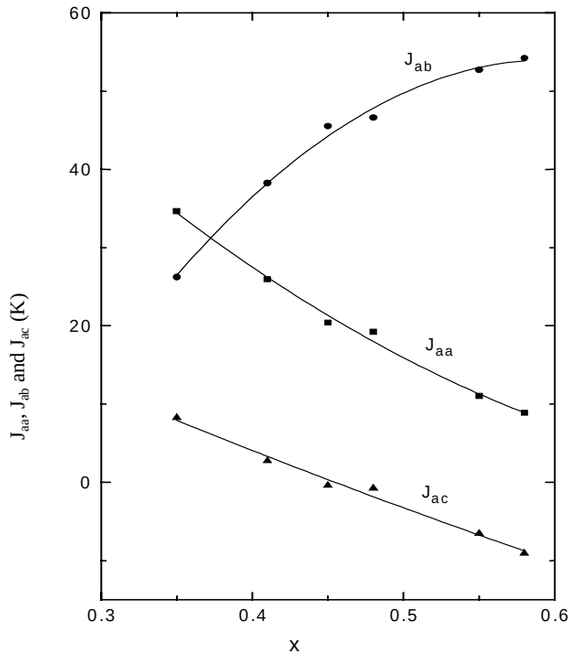

Figure 3 : Variation of the intra-plane, J_{aa} and inter-plane, J_{ab} and J_{ac} interactions with the ratio of dilution x in $Zn_xCd_{1-x}Cr_2Se_4$ in the range $0.35 \le x \le 0.58$.

For x=0.35 and 0.41, all the three interactions are positive. Thus, the system orders ferromagnetically. In the range $0.41 < x \le 0.58$, J_{ac} becomes more and more negative when x increases. This lead to the concept of frustration responsibles for the re-entrant behaviour in this

range of concentration. The ratio $\frac{|J_{ac}|}{4|J_{ab}|}$, reflecting the stability factor of the helimagnetic order, decreases when x increases and approaches the unity when approaching x=0.58. This show that in the range $0.41 < x \le 0.58$ the competition between the ferromagnetic nearest and antiferromagnetic next nearest inter-plane interactions is not sufficient to lead neither to a spin-glass state nor to helical order. But when x > 0.58, the helimagnetic phase would be stable. It is know from[21] that this order appears when we exceed x=0.58.

The high-temperature series expansion combined with the Padé approximant method allows as to have an independent determination of T_c. The values obtained are presented in Table 4. They are close to the experimental ones obtained by the scaling plot. The values of critical exponents γ and ν have been estimated in the range of concentration $0.35 \le x \le 0.58$. For the compound x=0.35 and x=0.41, we have obtained the central values of γ and ν, γ=1.381±0.014 and ν=0.694±0.011. These values may be compared with those of the 3D Heisenberg model, namely, 1.3866±0.0012 and 0.7054±0.0011 [22,23]. In the range of concentration $0.45 \le x \le 0.58$, γ and ν decrease with x from 1.381 to 0.942 for γ and from 0.694 to 0.553 for ν. It seems that these exponents describe a class of universality different from that of the ordered regions.

ACKNOWLEDGEMENTS

This work is supported by the "Comité Inter-Universitaire Maroco-Espagnole" under a grand N°: 62/SEE/98.

x	T_c(K)	γ[1,4]	γ[2,4]	γ[3,4]	γ[2,3]	γ[3,3]	ν[1,4]	ν[2,4]	ν[3,4]	ν[2,3]	ν[3,3]
0.35	67.5	1.396	1.394	1.391	1.383	1.381	0.715	0.712	0.704	0.697	0.694
0.41	57.8	1.395	1.393	1.390	1.383	1.382	0.716	0.714	0.702	0.695	0.693
0.45	52.5	1.391	1.376	1.374	1.370	1.375	0.703	0.698	0.696	0.691	0.687
0.48	48.5	1.265	1.260	1.254	1.250	1.246	0.680	0.676	0.685	0.673	0.671
0.55	39.8	1.102	1.103	1.095	1.081	1.070	0.626	0.620	0.618	0.613	0.612
0.58	33.5	0.991	0.996	0.969	0.948	0.942	0.606	0.585	0.566	0.577	0.553

Table 4 : The critical temperature T_c(±2.5 K) and the critical exponents γ (±0.014) for the magnetic susceptibility and ν(±0.011) for the correlation length deduced by applying differents [M,N] Padé approximant method. The values are calculated by considering the values of J_1 and J_2 given in Table 1.

[1] M. Hamedoun, A. Rachadi, A. Zerhouni, H. Lassri and M. Nogues, Physica B 229, 96 (1996)
[2] A. Belayachi, J. L. Dormann and M. Nogues, J. Phys. Cond. Matt. 10, 1599 (1998).
[3] E. Agostinelli, C. Battistoni, D. Fiorani, G. Mattogno and M. Nogues, J. Phys. Chem. Solid 50, 269, (1986).
[4] M. Nogues and J. L. Dormann, J. Mag. Mat. 54, 87 (1986).
[5] R. Plumier, C. R. Acad. Sci. (France) 260, 3348 (1965)
[6] P. K. Baltzer, H. W. Lehmann and M. Robbins, Phys. Rev. Lett. 15, 493 (1965).
[7] M. Hamedoun, A. Hourmatallah, A. Zerhouni, N. Benzakour, A. Belayachi and M. Nogues, Phys. Stat. Solid.(b) 203, 521 (1997).
[8] A. Hourmatallah, M. Hamedoun, A. Rachadi and N. Benzakour, Physica B 229, 256 (1997).
[9] R. Navaro, Magnetic Proprieties Of Layered Transition Metal Compounds, ed. by L. J. De Jongh (Daventa. Kluwer) 105 (1990).
[10] M. C. Moron, J. Phys : Condens. Mat. 8, 11141 (1996).
[11] F. K. Lotgering, Solid State Commun. 3, 647 (1965).
[12] G. Bush, B. Magyar and O. Vogt, Solid State Commun. 7, 509 (1969)
[13] W. E. Holland and H. A. Brown, Phys. Stat. Sol.(a) 10, 249 (1972).
[14] P. K. Baltzer, M. Robbins, and P. J. Wojtowicz, J. Appl. Phys. 38, 953 (1967).
[15] R. Plumier, Compt. Rend. 260, 3348 (1965); J. Appl. Phys. 37, 964 (1966).
[16] C. Guillaud, J. Phys. et radium, 12, 223 (1951).
[17] H.E. Stanley and T.A. Kaplan, Phys. Rev. Lett. 16, 981 (1966).
[18] M. Hamedoun, M. Houssa, N. Benzakour and A. Hourmatallah, J. Phy.: Condens. Matter 10, 3611 (1998).
[19] G. A. Baker, Phys. Rev. 124, 768 (1961).
[20] J. W. Essam and M. E. Fisher, J. Chem. Phys. 38, 802 (1963).
[21] R. Plumier, J. Phys. 27, 213 (1966).
[22] For a review, scc. Collins, M. F 1989, Magnetic. Critical. Scattering (Oxford: Oxford University Press).
[23] J. C. Le Guillou and J. Zinn-Justin, Phys. Rev. Lett. 2, 95 (1977).