

Study of the magnetic order in chromium spinel systems

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We present a study of the magnetic properties of the $A_{1-x}Cu_xCr_2X_4$ ($A=Cd, Zn, \dots; X=S, Se, O, \dots$) chromium spinel systems. Using the mean field theory, we have evaluated the nearest neighbour, the next-neighbour super-exchange, and the third next nearest neighbour interaction $J_1(x)$, $J_2(x)$ and $J_3(x)$, respectively for the $Zn_{1-x}Cu_xCr_2Se_4$ and $J_1(x)$, $J_2(x)$ for the $Cd_{1-x}Cu_xCr_2Se_4$ systems in the whole range of concentration $0 \leq x \leq 1$.

By using the high-temperature series expansions combined with the Padé approximants method, we have obtained the magnetic phase diagrams in T_C versus dilution x .

A spin glass phase is predicted for intermediate range of concentration. The obtained results are in agreement with experimental ones obtained by magnetic measurements for the systems studied. The critical exponents associated with the magnetic susceptibility χ and the correlation lengths ν have been deduced. The obtained values are comparable to those of 3D Heisenberg model, and are insensitive to the dilution x .

Keywords: Spinel, magnetic properties, exchange interactions, critical exponents, Phase diagrams.

PACS: 74.25.Ha; 71.71.Gm; 75.40.Cx; 71.10.Hf

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 $A_{1-x}Cu_xCr_2X_4$ ($A=Cd, Zn, \dots; X=S, Se, O, \dots$), where Cu and A ions occupy the tetragonal sites (A), while Cr ions occupy the octahedral sites (B) of normal spinel lattice.

The spinel systems $Zn_{1-x}Cu_xCr_2Se_4$ are normal spinels with strong preference of Cr ions to locate in the octahedral (B) positions. The stoichiometric compounds $ZnCr_2Se_4$ ($x=0$) and $CuCr_2Se_4$ ($x=1$) are, respectively, semiconductor with a magnetic spiral structure [4-5], (with spiral angle $\phi=42^\circ \pm 1^\circ$) and metallic ferromagnet [5,6]. The Néel temperature of the former is $T_N=22K$

($x=0$), while the Curie temperature of the latter is much higher and equal to $T_C=416K$ ($x=1$). As the

Cr-Cr distance ($d_{Cr-Cr}=3.53 \text{ \AA}$) in $ZnCr_2Se_4$ is intermediate between that of the oxyspinel and the seleno compounds it may be argued that the set of relevant exchange integrals are just at the transition line between the helical and the commensurate structure. The spinel $ZnCr_2Se_4$ system is semiconductive and shows an antiferromagnetic to paramagnetic phase transition at about $21K$. $CuCr_2Se_4$ is metallic and shows a ferromagnetic to paramagnetic phase transition at about $420K$. On the other hand, substitution of Zn with Cu ions gives a structural solid solution of the normal spinel structure [7] and causes fundamental changes of both magnetic and electrical properties. These systems are still the subject of

extensive experimental and theoretical studies [8-12] because:

- They exhibit both the transition from antiferromagnetic at $x=1$ through a conical structure from $x \leq 0.5$ to ferromagnetism at $x < 0.2$, and at the same time, a transition from semiconducting at $x=1$ to metallic phase of the p-type at $x < 0.8$.
- The experimental observed phase transitions from the magnetic ordered to the paramagnetic one induced by temperature.
- The magnetic properties are governed mainly by the narrow 3d band of chromium.

The systems $Cd_{1-x}Cu_xCr_2Se_4$ are normal spinels being ferrimagnetic p-type semiconductors for $x \leq 0.2$ and ferromagnetic p-type conductors for $x \geq 0.9$, [13-15]. In the case of the solid solutions $Cd_{1-x}Cu_xCr_2S_4$ (where $CdCr_2S_4$ is a Heisenberg ferromagnet with semi conductive p-type conductivity [16-18], and $CuCr_2S_4$ is a ferromagnet with the metallic p-type conductivity [19] one can obtain single- phase compounds only for Cu concentration $x \leq 0.2$ [20]. As it follows from the structural investigations, all the compounds under study normal spinels with the octahedral position occupied only by the Cr ions [21]. Lotgering [22] first studied magnetic and electrical properties of the compound $CuCr_2X$ ($X=S, Se$ and Te) with the normal spinel structure. It was found that these compounds exhibited metallic conduction and are ferromagnetic with a moment of about $5\mu_B$ per molecule. These compounds are ferromagnetic (FM) $T_C=420 K$ and $460 K$, and the Curie-Weiss temperature $\theta_p=390 K$ and $465 K$, respectively [23,24].

In recent works [25,26], we have used the high-temperature series expansions (HTSE) to study the thermal and disorder variation of the short-range order (SRO) in the particular B-spinel $Zn_{1-x}Cr_{2x}Al_{2-2x}S_4$ compound. Three first spin correlation functions have been calculated with the aid of the diagrammatic representation given by Stanley and Kaplan [27].

This paper concerns the interesting topic of magnetic structure and spin glass behaviour in the diluted spinel

$A_{1-x}Cu_xCr_2X_4$ ($A=Cd, Zn; X=S, Se$).

In these systems, the disorder is due to the magnetic ion Cr and in the system $Zn_{1-x}Cd_xCr_2S(Se)_4$ the disorder is due to the substitution between diamagnetic ions $Zn^{2+} \leftrightarrow Cd^{2+}$ on tetrahedral sites.

The Padé approximant (P.A) [28] analysis of the high-temperature series expansion (HTSE) of the correlation length has been shown to be a useful method for the study of the critical region [29,30]. We have used this technique to determine the critical temperature T_C and the critical exponents γ and ν associated with the magnetic susceptibility χ and the correlation length ξ respectively. The obtained theoretical phase diagrams are in rough qualitative.

II. Calculation of the values of the Exchange Integrals

Starting with the well known Heisenberg model, the Hamiltonian of the system is given by:

$$H = -2 \sum_{ij} J_{ij} \vec{S}_i \vec{S}_j \quad (1)$$

Where, J_{ij} is the exchange integral between the spins situated at sites i and j . \vec{S}_i is the operator of the spin localised at the site i . In this work we consider the nearest neighbour (nn), next nearest neighbour (nnn) and the third next nearest neighbour ($Tnnn$), J_1 , J_2 and J_3 respectively.

$$H = J_1 \sum_{ij} \vec{S}_i \vec{S}_j - J_2 \sum_{i,k} \vec{S}_i \vec{S}_k - J_3 \sum_{i,l} \vec{S}_i \vec{S}_l \quad (2)$$

The sums over ij , ik and il include all (nn), (nnn) and ($Tnnn$) pair interactions, respectively. In the case of spinels containing the magnetic moment only in the octahedral sublattice, the mean field approximation of this expression leads to simple relations between the paramagnetic Curie-temperature θ_p and the critical temperature T_C , the angle of helices ϕ , respectively, and the considered three exchange integrals J_1 , J_2 and J_3 .

Following, the method of Holland and Brown [31], the expressions of T_C and θ_p that can describe the system spinel are:

$$T_C = \frac{5}{2K_B} [2J_1 - 4J_2 - 4J_3] \quad (3)$$

$$\theta_p = \frac{5}{2K_B} [6J_1 + 12J_2 + 12J_3] \quad (4)$$

Where k_B is the Boltzmann constant.

Concerning the antiferromagnetic side, we have used the formula of Néel temperature T_N given by [7]:

$$T_N = \frac{2}{3} S(S+1) \lambda(\phi) \quad (5)$$

For helimagnetic B-spinel, the angle of helic ϕ [7], is given by:

$$\cos(\phi) = -\frac{1}{4} \frac{J_1 + 2J_2}{J_2 + 2J_3} \quad (6)$$

Using the experimental values of T_C , θ_p and ϕ for the $Zn_{1-x}Cu_xCr_2Se_4$ and T_C , θ_p for $Cd_{1-x}Cu_xCr_2Se_4$ systems given in reference [32,33], respectively. We have deduced the values of exchange integrals J_1 , J_2 and J_3 for the first and

J_1 , J_2 for the second systems for each composition x . The obtained optimum values are given in tables (1) and (2), respectively. The $J_1(x)$ and $J_2(x)$ will be used in the (HTSE) analysis. In the concentration range $0.2 \leq x \leq 1$ for the system $Cd_{1-x}Cu_xCr_2S_4$, we have used the values of J_1 , J_2 in the case pure.

x	$T_N(K)$ [30]	$T_C(K)$ [30]	θ_p [30]	ϕ [30]	$\frac{J_1}{K_B}$	$\frac{J_2}{K_B}$	$\frac{J_3}{K_B}$
0.00	22	-	118	42	16.89	-10.213	5.70
0.01	20	-	142	42	20.567	-12.783	7.232
0.02	16	-	188	41	27.523	-17.408	9.913
0.025	10	-	240	40	35.381	-22.559	12.868
0.05	14	-	276	37.5	40.167	-24.641	13.757
0.07	16	-	296	37	42.950	-26.140	14.531
0.1	20	-	332	36	47.868	-28.649	15.782
0.2		377	388	31	50.63	-23.99	11.613
0.3		382	391	26.5	51.233	-24.595	12.012
0.5		390	396	22.5	52.2	-25.42	12.52
0.7		395	411	11.5	53.2	-24.964	12.064
0.8		404	418	0	54.333	-25.766	12.533
0.9		408	427	0	55.033	-25.616	12.333
1		416	436	0	56.133	-26.066	12.533

Table 1: The Néel temperature $T_N(K)$, the critical temperature $T_C(K)$, the Curie-Weiss temperature θ_p , the angle of helic ϕ and the exchange interactions given by mean field theory of the system $Zn_{1-x}Cu_xCr_2Se_4$.

x	$T_{N,C}(K)$ [31]	θ_p [31]	$\frac{J_1}{K_B}$	$\frac{J_2}{K_B}$
0.00	86	133	13.03	-2.08
0.05	87	143	13.46	-1.96
0.10	85.5	200	15.21	-0.94
0.15	83.5	218	15.61	-0.54
0.2	81	283	17.53	0.66
1	420[17]	390[17]	55	-14.5

Table 2: The critical temperature $T_C(K)$, the Curie-Weiss temperature θ_p and the exchange interactions given by mean field theory of the system $Cd_{1-x}Cu_xCr_2S_4$.

III. High-temperature Series Expansions

In this section we shall derive the high-temperature series expansions (HTSE) for the both the zero field magnetic susceptibility χ and two-spin correlation functions ξ to order six in β . The relation ship

between the magnetic susceptibility per spin and the correlation functions may be expressed as follows:

$$\chi(T) = \frac{\beta}{N} \sum_{ij} \langle \vec{S}_i \vec{S}_j \rangle \quad (7)$$

Where $\beta = 1/k_B T$ and N is the number of magnetic ion. $\langle S_i S_j \rangle = \text{Tr} S_i S_j e^{-\beta H} / \text{Tr} e^{-\beta H}$ is the correlation function between spins at sites i and j . In [25], 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 high temperature series expansion of ξ^2 gives the function:

$$\xi^2(T) = \sum_{m=-n}^n \sum_{n=1}^6 b(m, n) y^m \tau^n \quad (8)$$

Where $y = J_2/J_1$ and $\tau = 2S(S+1)J_1/k_B T$. The series coefficients $b(m, n)$ are given in [34]. In spin-glasses critical behaviour near T_{SG} is expected not in the linear part χ_0 of the dc susceptibility χ ,

but in the nonlinear susceptibility $\chi_s = \chi - \chi_0$. This is due to the fact that the order parameter q in the spin glass state is not the magnetization but the quantity

$$q = \frac{1}{N} \sum_i \left[\langle S_i \rangle^2 \right]_{av}. \text{ As suggested by Edwards and Anderson [35], leading to an associated susceptibility}$$

$$\chi_s = \frac{1}{NT^3} \sum_{ij} \left[\langle S_i S_j \rangle^2 \right]_{av}, \text{ where the correlation}$$

length of the correlation function $\left[\langle S_i S_j \rangle^2 \right]$ possibly diverges at $T = T_{SG}$. The behaviour of the nonlinear susceptibility has been already extensively studied theoretically and experimentally [36, 37]. We have used the expression of χ_s , to determinate the critical temperature in the region of spin glass for the different spinels. Figs. 1-4 shows the phase diagrams of diluted

$$Zn_{1-x}Cu_xCr_2Se_4,$$

$$Zn_{1-x}Cr_{2x}Al_{2-2x}S_4 \text{ and}$$

$$Zn_{1-x}Cd_xCr_2Se_4 \text{ respectively. We can see}$$

the good agreement between the magnetic phase diagrams obtained by the HTSE technique and the experimental ones, in particular in the case of the last two systems of which the phase diagrams have been established well by different methods [38-40].

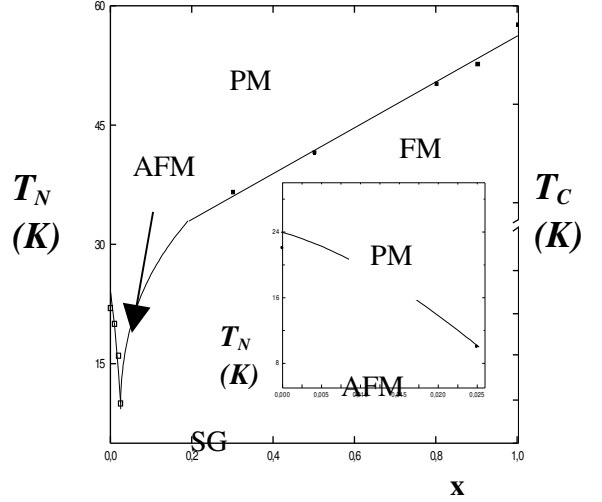


Fig. 1: Magnetic phase diagram of $Zn_{1-x}Cu_xCr_2Se_4$. The various phases are the paramagnetic phase (PM), the antiferromagnetic phase (AF) and the spin glass phase (SG). The solid lines are the present results. The dots represent the experimental points deduced by [32].

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

$$\chi(T) \propto (T - T_C)^{-\gamma} \quad (9)$$

$$\xi^2(T) \propto (T_C - T)^{-2\nu} \quad (10)$$

Estimates of T_C , γ and ν for $Zn_{1-x}Cu_xCr_2Se_4$ have been obtained using the Padé approximate method (PA) [28]. The simple pole corresponds to T_C and the residues to the critical exponents γ and ν . The obtained central values are $\gamma = 1.329 \pm 0.002$ and $\nu = 0.709 \pm 0.001$. The values of the critical exponents ν found by the different Padé are comparable with the one given on the other hand by Heisenberg model; the values found for γ are lower to the one of Heisenberg.

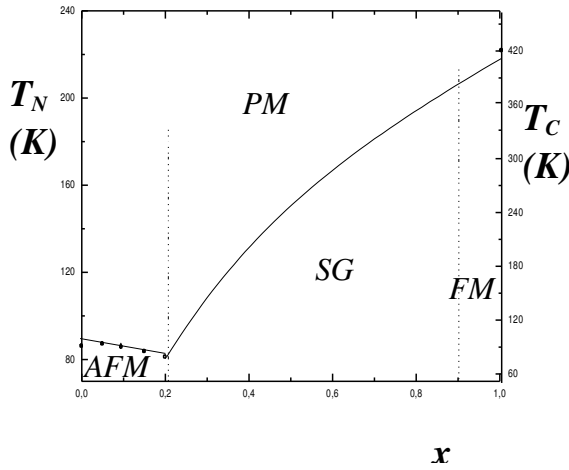


Fig. 2: Magnetic phase diagram of $Cd_{1-x}Cu_xCr_2S_4$. The various phases are the paramagnetic phase (PM), the antiferromagnetic phase (AF) and the spin glass phase (SG). The solid lines are the present results. The dots represent the experimental points deduced by [33].

V. Discussion and Conclusion

In the present work, we have used the experimental value of T_C , T_N , θ_p and ϕ to derive the three first exchange integrals $J_1(x)$, $J_2(x)$ and $J_3(x)$ for the $Zn_{1-x}Cu_xCr_2Se_4$ and T_C , θ_p to derive the $J_1(x)$, $J_2(x)$ for the $Cd_{1-x}Cu_xCr_2S_4$ systems for each dilution x .

The high-temperature series expansion (HTSE) extrapolated with Padé approximants method is shown to be a convenient method to provide valid estimations of the critical temperatures for real system. By applying this method to the magnetic susceptibility $\chi(T)$ and the correlation length $\xi(T)$ we have estimated the critical temperature T_C for each dilution x .

The obtained phase diagrams of the four spinels systems are presented in figures 1- 4. Several thermodynamic phases may appear including the paramagnetic (PM), antiferromagnetic (AF), ferromagnetic (F) and spin-glass (SG) phases. In these figures we have included, for comparison, the experimental results obtained by magnetic measurements given [32, 33, 38, 3]. From figures one can see good agreement between the theoretical phase diagram and experimental results.

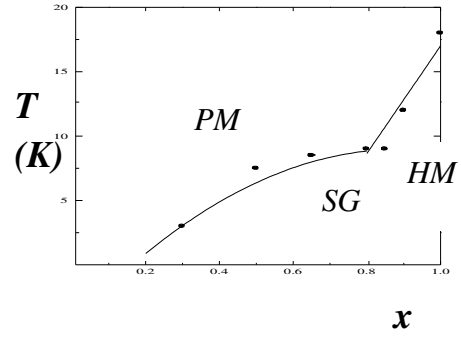


Fig. 3: Magnetic phase diagram of $ZnCr_{2x}Al_{2-2x}S_4$. The various phases are the paramagnetic phase (PM), the antiferromagnetic phase (AF) and the spin glass phase (SG). The solid lines are the present results. The dots represent the experimental points deduced by [38].

The spin glaze state of $ZnCr_{2x}Al_{2-2x}S_4$ and $Zn_{1-x}Cd_xCr_2Se_4$ (fig.3 and 4) has been experimentally obtained [38, 3]. Our theoretical method is in good accordance with the experimental data. In the case of the system $Zn_{1-x}Cu_xCr_2Se_4$ and $Cd_{1-x}Cu_xCr_2S_4$ (fig.1 and 2) there are no available experimental results. By the HTSE method we have obtained the phase diagram in the whole range of concentration ($0 \leq x \leq 1$).

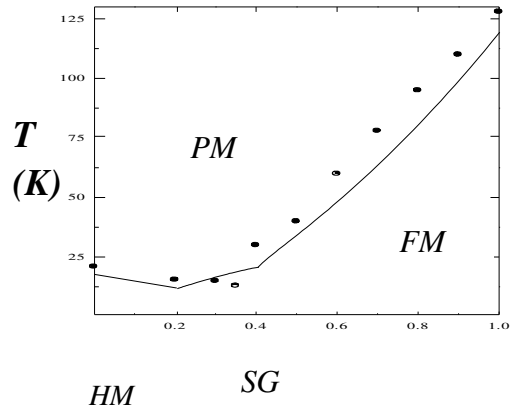


Fig. 4: Magnetic phase diagram of $Zn_{1-x}Cd_xCr_2Se_4$. The various phases are the precedent figure plus the ferromagnetic phase (FM). The solid lines are the present results. The dots represent the experimental points deduced from magnetic measurement [3].

In the other hand, the value of critical exponents associated to the magnetic susceptibility $\chi(T)$

and the correlation length $\xi(T)$, respectively, have been estimated in the range of the composition $0 \leq x \leq 1$. The sequence of [M, N] PA to series of $\chi(T)$ and $\xi(T)$ has been evaluated. By examining the behaviour of these PA, the convergence was found to be quite rapid. Estimates of the critical exponents associated with susceptibility and correlation length are found to be $\gamma = 1.329 \pm 0.002$ and $\nu = 0.709 \pm 0.001$, for the spinel $Zn_{1-x}Cu_xCr_2Se_4$. These values are insensitive to dilution x . They are comparable to those of 3D Heisenberg model.

Acknowledgements

This study is supported by the PROTARS III under grant N°: D12/10.

References

- [1] E. Agostinilli, C. Bahistoni, D. Fiorani, G. Maghogo, and M. Nougues, J.Phys.Chem-Solids **50**, (1986) 269.
- [2] M. Nougues, J. L. Dormann, J. Magn. Mater **87** (1986) 54.
- [3] M.Hamedoun, A. Zerhouni, A.Rachadi, M. Slimani and A. Benyoussef. Phys. Stats Sol (b) **192**, (1995)195.
- [4] R. Plumier, C. R. Acad.Sc **260**, (1965) 3348
- [5] F. K. Lotgering, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964*, (Institute of Physics, London, 1965), p.533.
- [6] R. Plumier, M. Lecomte, A. Miedan-Gros, M. Sougi, Phys. Lett A **55** (1975) 239.
- [7] M. Hamedoun, A.Rachadi, A. Hourmatallah, D.El Allam and A. Benyoussef, Phys. Stat Sol (b) **191**, (1995) 503.
- [8] S. Juszczuk, Physica B **161** (1989) 183.
- [9] S. Juszczuk, J. Magn. Mater. **83** (1990) 473.
- [10] M. N. Khan, A. Ventkatalachan, A. Ahmud, V. S. Darshane J.Mater. Sci. **25** (1990) 595.
- [11] Hidaka, N. Tokiwa, T. T. Wai, H. Fujii, K. Ohoyama, T. Mizushima, J. Sakurai, F. Ichikawa and K. Itoh, Phase Transitions **75** (2002) 273; Hidaka, N. Tokiwa, T. T. Wai, H. Fujii, M. Mitoh and K. Takeda, Applied Physics A Materials Science & Processing, **74** (2002) 820.
- [12] N. Tokiwa, M. Hidaka, physica status solidi (b) **241** (2004) 1910.
- [13] J. Krok - Kowalazki, H. Rej, T. Gron, J. Warczewski, T. Mydlarz and I. Okonska- Kozlowska, J. Magn. Mater, **137** (1994) 329.
- [14] J. Krok-Kowalski, J. Warczewski, and T. Mydlarz; J. Physique Suppl **49**, (1988) 881.
- [15] J. Krok-Kowalski, J. Warczewski, and J. Warczewski; J. Magn. Mater. **83** (1990) 367.
- [16] K. Baltzer, P. J. Wojtowicz, M. Robbim and E. Lopatin, Phys. Rev B **151** (1966) 367.
- [17] N. Menyik and K. Dwight, J. Phys. Chem. Solids **29** (1968) 819.
- [18] S. Kubiak, W. Zarek, Z. Drzazga, J. Krok and A. Chelkowski, Acta Phys. Polon A **45** (1974) 819.
- [19] F. K. Lotgering, *Proc. Int. Conf. On Magnetism, Nottingham* (1964) P. **533**.
- [20] H. D Lutz, V. Koch and I. Okonoska- Kozlowska, J. Sol. Chem **51** (1984) 69.
- [21] H. Rej, J. Warczewski and I. Okonoska, Mater Sci-Froum **133** (1993) 733.
- [22] F. K. Lotgering: *Proc. Intern. Conf. on Magnetism* (1964) p. 533.
- [23] T. Kanomata, Hideaki Ido and T. Kaneko, J. Phys. Of Japan, Vol. **29** (1970), 332
- [24] I. Okonska-Kozlowska, J. Kopyczok, H. D. Lutz, Th. Stingl, Acta Crystallogr. C **49** (1993) 1448.
- [25] M. Hamedoun, M. Houssa, N. Benzakour and A. Hourmatallah, J. Phys.: Condens. Mater. **10** (1998) 3611.
- [26] M. Hamedoun, M. Houssa, N. Benzakour, A. Hourmatallah, Physica B **270** (1999) 384.
- [27] H. E. Stanley, Phys. Rev. **158** (1967) 537, H. E. Stanley, T. A. Kaplan, Phys. Rev.Lett. **16** (1966) 981.
- [28] "Padé Approximants", edited by G. A. Baker and P. Graves-Morris (Addison-Wesley, London, 1981).
- [29] R. Navaro, Magnetic Properties of Layered Transition Metal Compounds, Ed. L.J.DE Jonsgh, Daventa: Kluwer 1990 (p.105).
- [30] M. C. Moron, J. Phys: Condensed Matter **8** (1996) 11141.
- [31] W. E. Holland and H. A. Broun, Phys-Stat. Sol (a) **10** (1972) 249.
- [32] J. Krok, J. Spalek, S. Juszczuk and J. Warczewski, Phys. Rev. B **28** (1983) 6499.
- [33] J. Krok-Kowalski, T. Gron, J. Warczewski, T. Mydlarz, I. Okonska-Kozlowska, J. Magn. Mater. **168** (1997)129.
- [34] N. Benzakour M. Hamedoun, M. Houssa, A. Hourmatallah, and F. Mahjoubi, Phys. Stat. Sol. (b) **212** (1999) 335.
- [35] S. F. Edwards and P. W. Anderson, J. Phys. F **5**, (1975) 965.
- [36] S. Katsura, Prog, Theo. Phys. **55**, (1976) 1049.
- [37] G. Toulouse and M. Gabay, J. Phys. Lett. **42**, (1981) L 103
- [38] M. Alba, Hammann and M. Nougues, J. Phys, C **15** (1982) 5441.
- [39] K. Afif, A. Benyoussef, M. Hamedoun and A. Hourmatallah, Phys. Stat. Sol (b) **219** (2000) 383.
- [40] M. Hamedoun, M. Hachimi, A. Hourmatallah and K. Afif, J. Magn. Mater **283** (2001) 290.
- [41] W. Zarek, Acta. Phys. Polon. A **52** (1977) 657.
- [42] S. Sarbach, J. Phys. C **13**, (1980) 5033.