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# Magnetic behaviour and critical phenomenon in spinels $x$CuCr$_2$Se$_4$ -(1-$x$)Cu$_{0.5}$Ga$_{0.5}$Cr$_2$Se$_4$ systems

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**Abstract** - We studied the magnetic properties and the critical behaviour of the $xCuCr_2Se_4$-$(1-x)Cu_{0.5}Cr_2Se_4$ systems in the range $0 \le x \le 1$. The values of the nearest neighbouring ($J_1$) and next-nearest neighbouring ($J_2$) exchange interactions are calculated by a probability law adapted of the nature of dilution problem in B-spinel lattice.The high-temperature series expansions have been applied in the spinels $xCuCr_2Se_4$-$(1-x)Cu_{0.5}Cr_2Se_4$ systems, combined with the *Padé* approximants method, to determine the critical temperature ($T_C$) in the range $0 \le x \le 1$. The magnetic phase diagram, i.e. $T_C$ versus dilution $x$, is obtained. The critical exponents associated with the magnetic susceptibility ($\gamma$) and the correlation lengths ($\nu$) in region order are deduced in the range $0.2 < x \le 1$. The obtained values of $\gamma$ and $\nu$ are insensitive to the dilution ratio $x$ and may be compared with other theoretical results based on 3D Heisenberg model.

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## 1. Introduction

Materials with spinel structures are of continuing interest because of their wide variety of physical properties. This essentially related to: (i) the existence of two types of crystallographic sublattices, tetrahedral (A) and octahedral (B), available for the metal ion; (ii) the great flexibility of the structure in hosting various metal ions, differently distributed between the two sublattices, with a large possibility of reciprocal substitution between them. The spinels $xCuCr_2Se_4-(1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$ systems in the range $0 \le x \le 0.1$ is semiconductor with magnetic properties characteristic of spin glass and in the range $0.1 < x \le 1$, this compound exhibits a ferromagnetic order [1]. $Cu_{0.5}Ga_{0.5}Cr_2Se_4$ was the first gallium-doped chalcogen spinel which has been investigated in detail [2]. These investigations revealed its semiconducting and spin-glass like properties [2,3]. Later, some phase relationships of the $Cu_{1-x}Ga_xCr_2Se_4$ spinel system were found [3] and the growth conditions of the single crystals were established [4,5]. The end member of this spinel system, i.e. $CuCr_2Se_4$ exhibits a p-type metallic conductivity with the chromium spins coupled ferromagnetically via double exchange interaction involving the electrons jumping between $Cr^{3+}$ and $Cr^{4+}$ ions [6-8].

In this work, the values of the nearest neighbouring ($J_1$) and next-nearest neighbouring ($J_2$) exchange interactions are calculated, by a probability law in the range $0 \le x \le 1$.

The *Padé* approximant (P.A) [9] analysis of the high-temperature series expansions (HTSE) of the correlation functions has been shown to be a useful method for the study of the critical region [10,11]. We have use this technique to determine the critical temperatures $T_C$ or freezing temperature $T_{SG}$ and the critical exponents $\gamma$ and $\nu$ associated with the magnetic susceptibility $\chi(T)$ and the correlation length $\xi(T)$, respectively. The series expansions for the susceptibility $\chi(T)$ and for the correlation length $\xi(T)$ have been derived to the order sixth in the reciprocal temperature for the B-spinel lattices including both nearest-neighbouring $(nn)$ and next-nearest-neighbouring $(nnn)$ interactions in the Heisenberg model. Estimates values of critical temperature $T_C$ and critical exponents $\gamma$ and $\nu$ for the spinels $xCuCr_2Se_4-(1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$ systems are given in the range $0.1 < x \le 1$. The freezing temperature $T_{SG}$ is given in the range $0 \le x \le 0.1$.

## 2. Calculation of the values of the exchange integrals

In the diluted spinels $A_xA'_{1-x}B_2X_4$ systems, only the random placement of the diamagnetic ions A and A’ leads to the spatial fluctuations of the signs and magnitudes of the super-exchange interaction between the magnetic ions B. Indeed, the magnetic order is very sensitive to the distance between nearest neighbouring B ions and to the size of the anions A and A’. Due to the nature of dilution problem we choose a probability law permitting us to determine exchange integral $J_{AA'}(x)$ for each concentration $x$. The two exchange integrals of the opposite pure compound $AB_2X_4$ and $A'B_2X_4$ of the bound random spinel are denoted $J_A$ and $J_{A'}$ respectively. The occupation probability $p(i)$ of the two ions A or A’ induced in the interaction is $p(i) = C_n^i x^{n-i}(1-x)^i$, where n is considered as the number of cations situated in tetrahedral sites at the same distance n =6 while $i$ varies from 1 to 6. The exchange integral for such an occupation is assumed to be: $J_{AA'}^i = (J_A^{n-i}J_{A'}^i)^{1/n}$. The expression obtained by Ref [12] is:

$$
\begin{aligned}
J_{AA'}(x) &= x^6 J_A + 6x^5(1-x)\left(J_A{}^5 J_{A'}\right)^{1/6} + 15x^4(1-x)^2 \\
&\left(J_A{}^4 J_{A'}{}^2\right)^{1/6} + 20x^3(1-x)^3\left(J_A{}^3 J_{A'}{}^3\right)^{1/6} + 15x^2(1-x)^4 \\
&\left(J_A{}^2 J_{A'}{}^4\right)^{1/6} + 6x(1-x)^5\left(J_A J_{A'}{}^5\right)^{1/6} + (1-x)^6 J_{A'}
\end{aligned}
\tag{1}
$$

If $J_A(J_{A'})$ corresponds to the $nn$ interactions of the opposite pure systems $AB_2X_4\left(A'B_2X_4\right)$. $J_{AA'}(x) = J_1(x)$ and if $J_A(J_{A'})$ corresponds to the $nnn$ super-exchange of the opposite pure systems $J_{AA'}(x) = J_2(x)$.

$xCuCr_2Se_4-(1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$ is diluted spinels systems of $CuCr_2Se_4$ with $nn$ exchange integral $J_1 = 56.133\ K$ and $nnn$ super-exchange integral $J_2 = -13.533K$ [13] and for $Cu_{0.5}Ga_{0.5}Cr_2Se_4$ we have obtained $J_1 = 37.2\ K$ and $J_2 = 11.4K$ [1]. The obtained values of $J_1$ and $J_2$ are given in the Table 1, for $0 \le x \le 1$. The values of $J_1(x)$ and $J_2(x)$ will be used in section 3.

Table 1: The exchange integrals of $xCuCr_2Se_4$ - $(1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$ as a function of dilution $x$.

| $x$ | $T_C(K)$ [1] | $T_{SG}(K)$ [1] | $T_C(K)$ Present work | $T_{SG}(K)$ Present work | $\frac{J_1}{k_B}(K)$ | $\frac{J_2}{k_B}(K)$ |
|---|---|---|---|---|---|---|
| 0.03 | - | 8.6 | - | 8 | 37.677 | -11.459 |
| 0.05 | - | 11.7 | - | 10 | 37.999 | -11.499 |
| 0.1 | - | 19.5 | - | 17 | 38.812 | -11.599 |
| 0.125 | 34 | - | 30 | - | 39.224 | -11.650 |
| 0.15 | 56 | - | 50 | - | 39.640 | -11.700 |
| 0.2 | 78.5 | - | 72 | - | 40.482 | -11.802 |
| 0.3 | - | - | 345 | - | 42.212 | -12.008 |
| 0.4 | - | - | 356 | - | 44.003 | -12.216 |
| 0.5 | - | - | 367 | - | 45.857 | -12.428 |
| 0.6 | 385 | - | 380 | - | 47.77 | -12.64 |
| 0.7 | 374 | - | 379 | - | 49.761 | -12.86 |
| 0.8 | 427 | - | 423 | - | 51.814 | -13.08 |
| 0.9 | 425 | - | 420 | - | 53.937 | -13.305 |
| 1 | 416[6] | - | 412 | - | 56.133 | -13.533 |

## 3. High-temperature series expansions

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

$$H = -2\sum_{i,j} J_{ij}\vec{S}_i\vec{S}_j \tag{2}$$

where $J_{ij}$ is the exchange integral between the spins situated at sites *i* and *j*. $\vec{S}_i, \vec{S}_j$ is the operator of spin at site $i$ and $j$.

The relationship between the magnetic susceptibility per spin $\chi(T)$ and the correlation functions may be expressed as follows:

$$\chi(T) = \frac{\beta}{N}\sum_{ij}\left\langle \vec{S}_i\vec{S}_j \right\rangle \tag{3}$$

where $\beta = 1/k_B T$ , N is the number of ions and

$$\left\langle \vec{S}_i\,\vec{S}_j \right\rangle = Tr\vec{S}_i\vec{S}_j e^{-\beta H} / Tre^{-\beta H} \tag{4}$$

is the correlation function between spins at sites *i* and *j*. The expansion of this function in powers of $\beta$ is obtained as follows [14]:

$$\left\langle \vec{S}_i \vec{S}_j \right\rangle = \sum_{l=0}^{\infty} \frac{(-1)^l}{l!} \alpha_l \beta^l \tag{5}$$

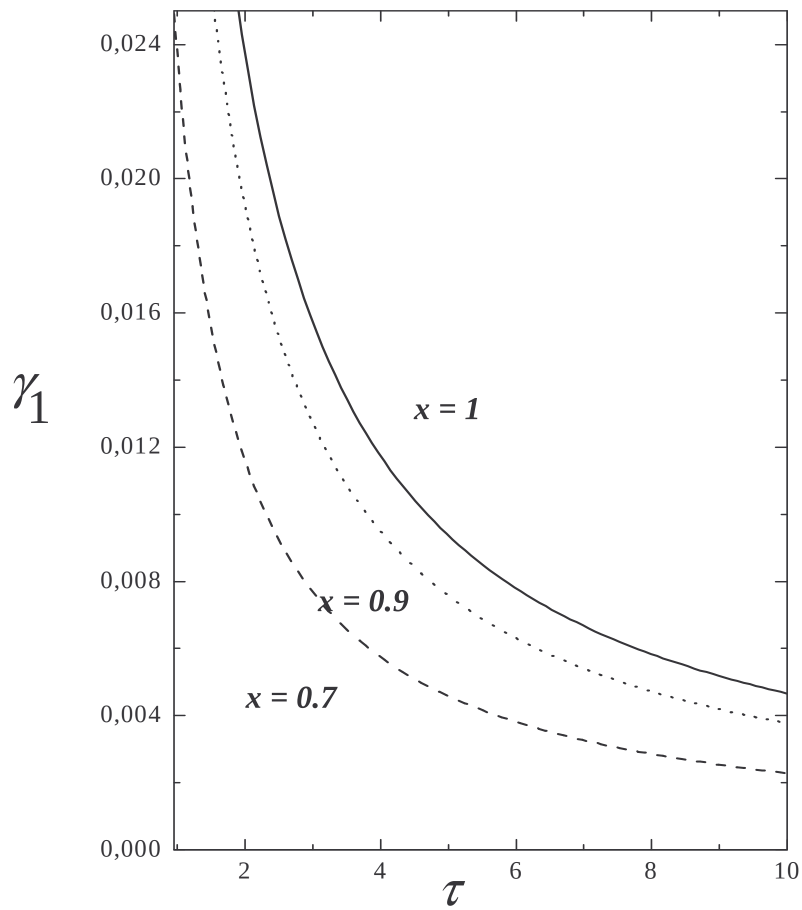


Fig. 1. The first-nearest-neighbour spin correlation function $\gamma_1$ plotted against the reduced temperature for the spinels $xCuCr_2Se_4-(1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$ systems for $x=0.7,\ 0.9$ and 1.

In the previous work, [14] the coefficient $\alpha_l$ required for the calculation of the three first correlation functions in the case of the B-spinel lattice are given. The HTSE are developed for $\chi(T)$ up to sixth order in $\beta$:

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

where $\tau = \dfrac{2S(S+1)J_1}{k_B T}$, $g$ is the Landé factor, $y = J_2/J_1$, $\mu_B$ is the Bohr magneton, $k_B$ is Boltzmann's constant and the series coefficients $a(m,n)$ were given in Ref. [15]. Eq. (5) permits the computation of the spin correlation functions $\gamma_i(i=1,\ 2)$ in terms of powers of $\beta$ and $x$ mixed $J_1$ and $J_2$. Figs 1 and 2, shows the variation of the first and the second correlation functions with the reduced temperature for $x=0.7,\ 0.9$ and 1, respectively.

In the previous works, [16] 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 expansions of $\xi^2$ to order sixth in $\beta$ gives the function:

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

with the series coefficients $b(m,n)$ were given in Ref. [15].

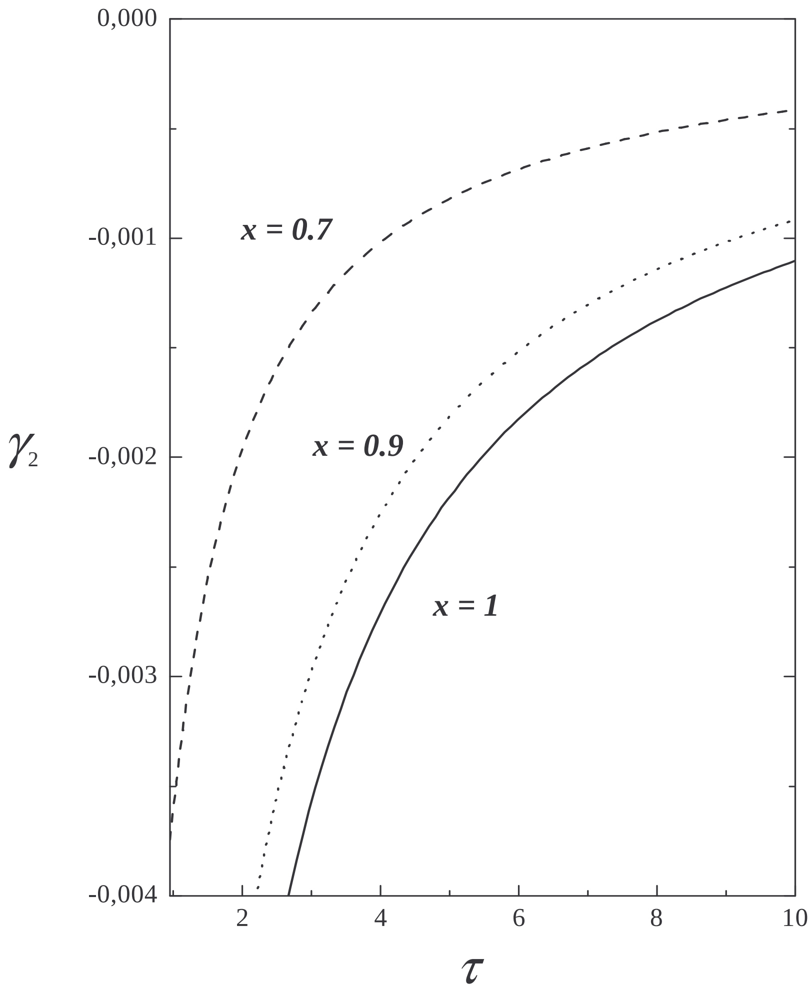


Fig. 2. The second-nearest-neighbour spin correlation function $\gamma_2$ plotted against the reduced temperature for the spinels $xCuCr_2Se_4-(1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$ systems for $x=0.7$, $0.9$ and $1$.

In the spin-glass (SG) region, critical behaviour near the freezing temperature $T_{SG}$ is expected in the nonlinear susceptibility $\chi_s=\chi-\chi_0$ rather than in the linear part $\chi_0$ of the dc susceptibility $\chi$. This is due to the fact that the order parameter $q$ in the SG state is not the magnetization but the quantity $q=\frac{1}{N}\sum_i\left[\langle S_i\rangle^2\right]_{EA}$. As was suggested by Edwards and Anderson, [17] leading to an associated susceptibility $\chi_s = \frac{1}{NT^3}\sum_{ij}\left[\left\langle s_i s_j \right\rangle^2\right]_{EA}$, where the correlation length of the correlation function $\left[\left\langle S_i S_j \right\rangle^2\right]$ possibly diverges at $T = T_{SG}$.

Fig 3, shows magnetic phase diagram of spinels $xCuCr_2Se_4 - (1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$ systems. We can see the good agreement between the magnetic phase diagram obtained by the HTSE technique and the experimental ones, in particular in the case of the last systems of which the phase diagram have been established well by different methods [18-22].

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 the following functions exhibit the asymptotic behaviour:

$$\chi(T) \propto (T - T_C)^{-\gamma} \tag{8}$$

$$\xi^2(T) \propto (T_C - T)^{-2\nu} \tag{9}$$

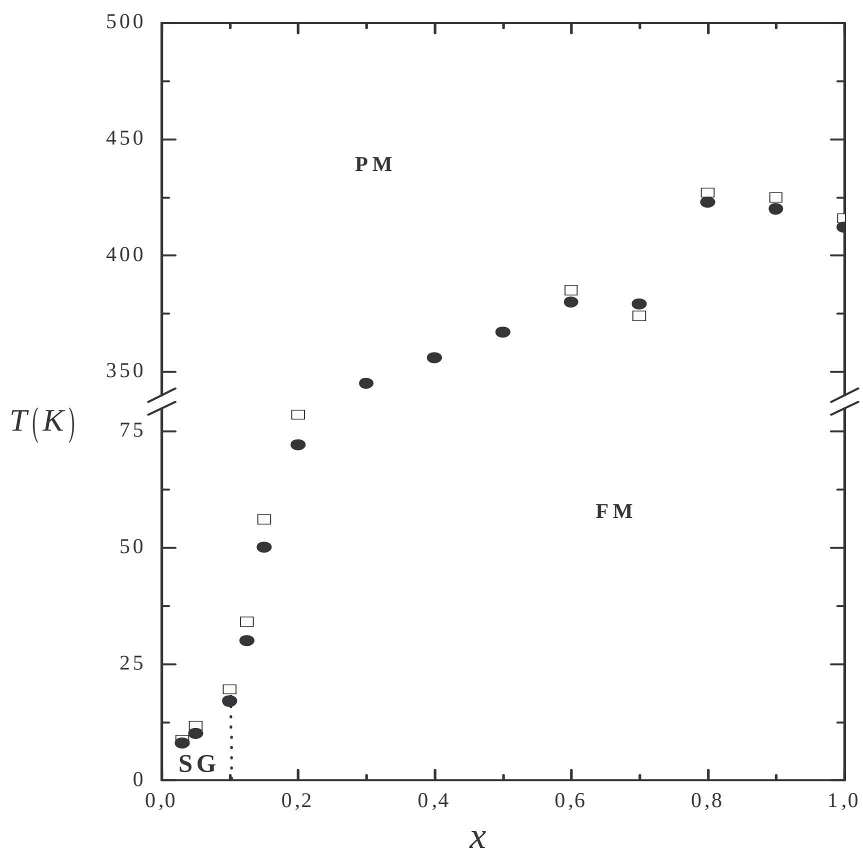


Fig. 3. Magnetic phase diagram of $xCuCr_2Se_4 - (1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$. The various phases are the paramagnetic phase (PM), ferromagnetic phase (FM) $(0.1 < x \le 1)$ and the spin glass state (SG)$(0 \le x \le 0.1)$. Solid circles show, the represent results. Open squares represent the experimental data deduced by magnetic measurements [1].

Estimates of $T_C$ or $T_{SG}$, $\gamma$ and $\nu$ for $xCuCr_2Se_4-(1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$ have been obtained using the P.A method [9]. The simple pole corresponds to $T_C$ and the residues to the critical exponents $\gamma$ and $\nu$. The obtained central values of $\gamma$ and $\nu$ in the ordered regions are: $\gamma = 1.383$ and $\nu = 0.694$. In disorder to determine $T_{SG}$, we have applied the PA method to the expression of $\chi_s$.

**4. Discussions and conclusions**

In this work, we have used a probability law adapted of the nature of dilution problem to determine the neighbouring nearest and next-nearest neighbouring exchange interactions $J_1(x)$ and $J_2(x)$, respectively, for $xCuCr_2Se_4-(1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$ systems. The obtained values are given in table 1 in the range $0 \leq x \leq 1$. The sign of $J_1(x)$ and $J_2(x)$ are positive and negative, respectively in the range $0 \leq x \leq 1$. From the table 1, on can see that $J_1(x)$ and $J_2(x)$ increases with the absolute value when $x$ increases. The system remains ferromagnetic in range $0.1 < x \leq 1$ because this solid solution is rich with the constituent $CuCr_2Se_4$, which is the ferromagnetic compound. The substitution of $CuCr_2Se_4$ by the spin-glass compound $Cu_{0.5}Ga_{0.5}Cr_2Se_4$ affects clearly the strength of the magnetic interaction $Cr^{3+}-Cr^{3+}$ in the constituent $CuCr_2Se_4$. In the range $0.1 < x \leq 1$, the magnetic properties of the spinels $xCuCr_2Se_4-(1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$ systems are principally dominate by the ferromagnetism of the $CuCr_2Se_4$. The behavior of the spin correlation functions $\gamma_1$ and $\gamma_2$ (see Figs 1 and 2) deduced from the Eq(5). From the Fig 1, on can see that $\gamma_1$ increases with the value when $x$ increases. In the Fig 2, on case see that $\gamma_2$ increases with the value when $x$ decreases and is negative for all dilution. We note that the main term of the spin correlation function ($\gamma_i$) is proportional to the exchange interaction $J_i$.

The 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 $\chi(T)$, we have estimated the critical temperature $T_C$ (in the ordered phase) or the freezing temperature $T_{SG}$ (in the ordered phase) for each dilution $x$ in the spinels $xCuCr_2Se_4-(1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$ systems. The obtained magnetic phase diagram of spinels $xCuCr_2Se_4-(1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$ systems is presented in Fig 3. Several thermodynamic phases may appear including the paramagnetic (PM) and the ferromagnetic (FM) in the range $0.1 < x \leq 1$ and spin glass (SG) in the range $0 \leq x \leq 0.1$. In the other hand, the value of critical exponents $\gamma$ and $\nu$ associated to the magnetic susceptibility $\chi(T)$ and the correlation length $\xi(T)$, have been estimated in the ordered regions. 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 magnetic susceptibility and the correlation length for the spinels $xCuCr_2Se_4-(1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$ systems are found to be $\gamma = 1.383$ and $\nu = 0.694$.

In other hands, the values of critical exponents $\gamma$ and $\nu$ associated to the magnetic susceptibility $\chi(T)$ and the correlation length $\xi(T)$, respectively, have been estimated in the range $0.1 < x \leq 1$ and for several [M, N] P.A. The convergence is extremely good and from the elements near to and on the diagonal of P.A [M, N]. We estimate the central value of the critical exponents: $\gamma = 1.383$ and $\nu = 0.694$. The values of $\gamma$ and $\nu$ are nearest to the one of 3D Heisenberg model [23], namely, $1.3866 \pm 0.0012$, $0.7054 \pm 0.0011$ and insensitive to the dilution. To conclude, it would be interesting to compare the critical exponents $\gamma$ with other theoretical values. A lot of methods of extracting critical exponents have been given in the literature. We have selected many of the methods, and summarised our findings below. In the critical region, i.e. $5\times10^{-4} \le \frac{(T_C - T)}{T_C} \le 5\times10^{-3}$, Zarek [24] has found experimentally by magnetic balance for $CdCr_2Se_4$ is $\gamma = 1.29 \pm 0.02$; for $HgCr_2Se_4$ $\gamma = 1.30 \pm 0.02$ and for $CuCr_2Se_4$ is $\gamma = 1.32 \pm 0.02$.

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