Magnetic studies and critical behaviour in $Zn_xCd_{1-x}Cr_2Se_4$ compounds ($0.35 \leq x \leq 0.45$)

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

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

Magnetization measurements were presented in this paper for the spinel solid solutions $Zn_xCd_{1-x}Cr_2Se_4$ for $x = 0.35$, 0.41 and 0.45. The Cr moment is 2.8 μ_B/Cr where the magnetization saturates for fields up to 10 kOe at low temperature. The ferromagnetic scaling properties permit to determine the critical temperature T_c 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 $\gamma = \beta(\delta - 1)$ 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 (tnn).

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 $Zn_xCd_{1-x}Cr_2Se_4$, 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 $x = 0$ [4] to insulating and complex antiferromagnet [5] with a helical spin structure for $x = 1$ [6]. In an intermediate range of composition ($0.45 < x < 0.49$) a spin-glass-like behaviour has been observed [2].

The purpose of this paper is to study the properties derived from magnetic isotherms in the asymptotical critical region ($T \approx T_c$) for the concentration x = 0.35, 0.41 and 0.45. As was reported in [3] 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 T_c , the critical exponents β for the spontaneous magnetization (M), γ for the susceptibility (χ) and δ for the magnetization at $T = T_c$ several curves representing the field (H) dependence of the magnetization are performed on the three compounds at different temperatures close to T_c.

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

$Zn_xCd_{1-x}Cr_2Se_4$ 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 Cr_2Se_3. 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 $\pm$0.02 K. The relative error of the magnetization and field measurements was estimated to be less than 5%.

III. RESULTS

A. Determination of T_c by magnetic measurements and Arrot plot method

Figure 1 shows the field dependence of the magnetization for $Zn_{0.35}Cd_{0.65}Cr_2Se_4$ at different temperatures. In order to evaluate the Cr moment, let us examine the results at 4.2 K.

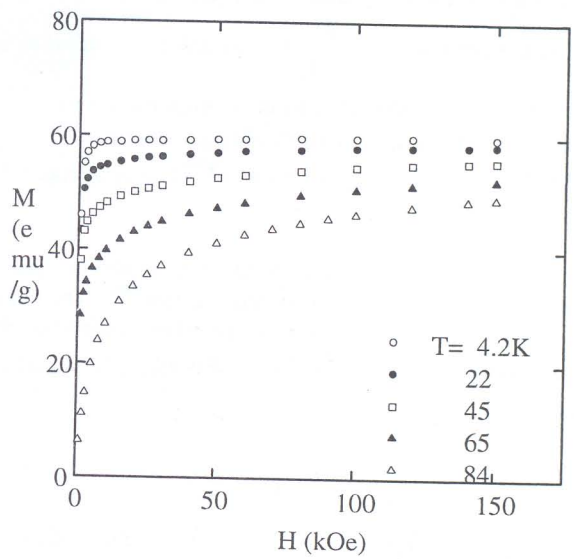

Fig. 1. The field dependence of the magnetization for $Zn_{0.35}Cd_{0.65}Cr_2Se_4$ at different temperatures.

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 /Cr. This value is not very different from the theoretical value $g\mu_B S$ 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=0.1T 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.

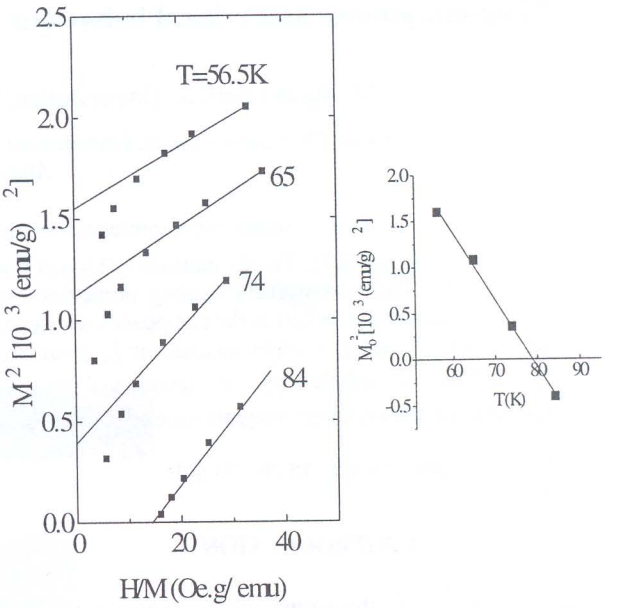

FIG. 2: The Arrot plots for the compounds $Zn_{0.35}Cd_{0.65}Cr_2Se_4$ (The inset shows M_o^2 versus T).

B. Determination of T_c and β, γ and δ by the scaling plot method

As an example, the measured magnetization M as a function of the internal field Hi (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 [7-8] that the second order phase transition around the temperature T_c is characterised by a set of critical exponents β, γ and δ 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 $H_i^{\frac{1}{\delta}}$.

The scaling plot is a useful method to study the phase transition in ordered and disordered systems [9-10]. The static scaling law [7-11-12] gives the following relation between the critical exponents : $\gamma = \beta(1+\delta)$ and a magnetic equation of state given by :

$$\frac{M}{|t|^{\beta}} = f_{\pm}\left(\frac{H_i}{|t|^{\beta+\gamma}}\right) \qquad (1)$$

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: $f_-(h_i)$ for temperatures below T_c and $f_+(h_i)$ for temperatures above T_c.

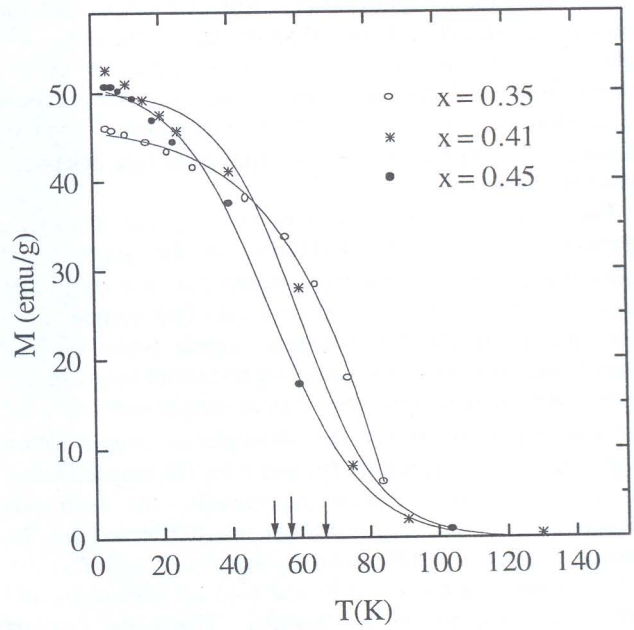

FIG. 3: Temperature dependence of the magnetization at low field (H=0.1T) for x=0.35 , 0.41 and 0.45. The arrows show the critical temperature T_c .

In practice, using a computer program, the transition temperature from the magnetic measurements [2] was varied in a ±2 K range. The values of β and γ 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 δ, 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 δ was deduced, as shown in Fig. 6 for x = 0.45.

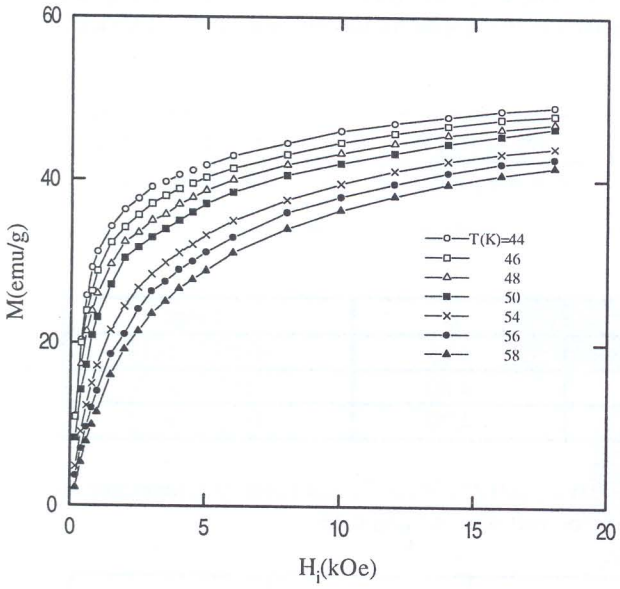

FIG. 4: Internal field dependence of the magnetization at various temperatures in the system $Zn_{0.45}Cd_{0.55}Cr_2Se_4$.

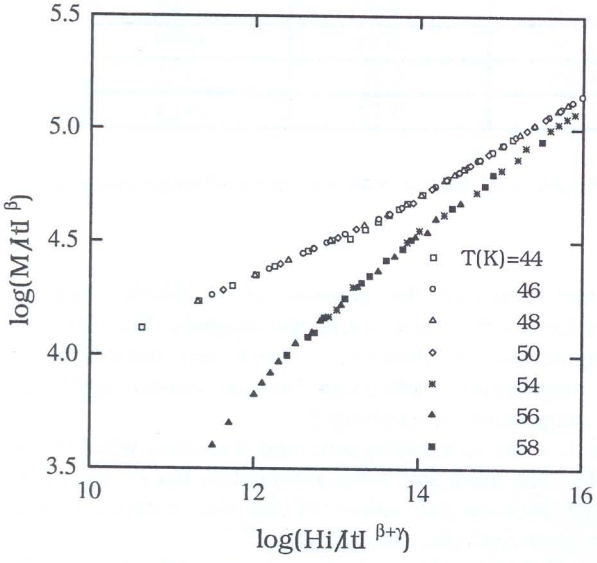

FIG. 5: Scaling plot of the magnetic isotherms in logarithmic form over the field range 0.1—18 kOe below and above Curie temperature for the $Zn_{0.45}Cd_{0.55}Cr_2Se_4$.

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.

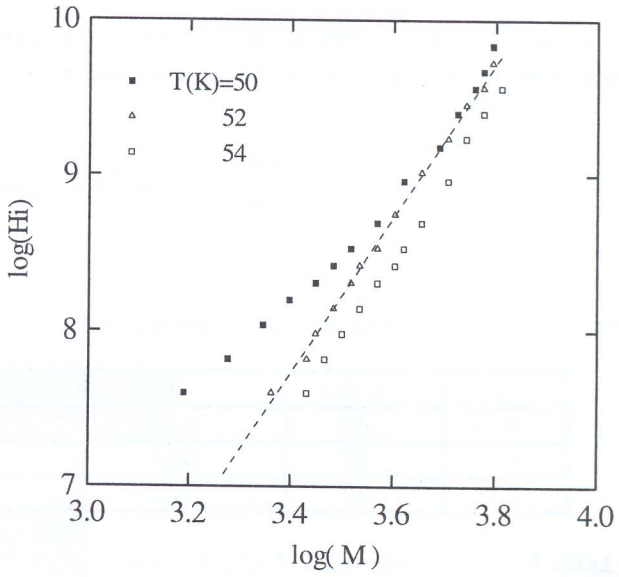

FIG. 6: *Log-log* plot of the magnetic isotherms for $Zn_{0.45}Cd_{0.55}Cr_2Se_4$ around and at T_c. The dashed line corresponds to the adjusted power law.

IV. CALCULATION OF THE VALUES OF THE EXCHANGE INTEGRALS

The model used is the classical Heisenberg hamiltonian:

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

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 $Zn_xCd_{1-x}Cr_2Se_4$ is :

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

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 θ_p and the exchange integrals [15]:

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

The experimental values of θ_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 $T^{\frac{3}{2}}$ shows very clearly that

the Bloch's law $M(T) = M(0)[1 - BT^{\frac{3}{2}}]$ holds in a large range of temperature and the coefficient B is given for x = 0.35, 0.41 and 0.45 .

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.

$$B = \frac{1.87}{QS}\left(\frac{k_B}{2S(J_1 + 10J_2 + 12J_3)}\right)^{3/2} \frac{1}{\left\{1 - \frac{48(J_2 + J_3)^2}{(J_1 + 10J_2 + 12J_3)^2} - \frac{128(J_2 + J_3)^3}{(J_1 + 10J_2 + 12J_3)^3}\right\}^{1/2}} \quad (5)$$

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

x	T_c (K)	β	γ	δ	t range
0.35	66	0.40	1.50	4.85	-0.09 — 0.13
0.41	58	0.40	1.50	4.80	-0.1— 0.15
0.45	52	0.42	1.55	4.70	-0.15 — 0.12

Table 1. Critical temperature T_c (± 2 K), critical exponents β (±0.04), γ(±0.25), δ (±0.3) and reduced temperature range t used in ferromagnetic scaling plots for the system $Zn_xCd_{1-x}Cr_2Se_4$ for x=0.35, 0.41 and 0.45.

x	θ_p (K) [16]	$B(10^{-5}K^{-3/2})$ [17]	$\frac{J_1}{k_B}(K)$	$\frac{J_2}{k_B}(K)$	$\frac{J_3}{k_B}(K)$
0 [18]	-	-	14	-0.10	-
0.35	172.80	63.30	12.36	-2.90	2.48
0.41	167.40	73.30	11.38	-0.91	0.80
0.45	163.80	76.70	10.66	0.36	-0.23
1 [19]	-	-	9.94	3.12	-4.26

Table 2. Curie-Weiss temperature θ_p , Bloch's coefficient B and values of the nn, nnn and tnn exchange integrals of $Zn_xCd_{1-x}Cr_2Se_4$ as a function of the dilution x.

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

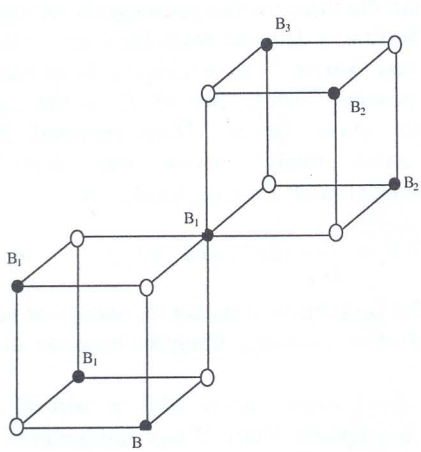

FIG. 7: Portion of spinel lattice showing the nn (B_1), nnn (B_2) and tnn (B_3) of the magnetic ion B.

V. DISCUSSION

In diluted $Zn_xCd_{1-x}Cr_2Se_4$ compounds, we have used the values of the critical temperature T_c derived from the scaling plot, the asymptotic Curie-Weiss temperatures θ_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 $ZnCr_2Se_4$ and $CdCr_2Se_4$ [18-19].

J_1 may be affected by a slight variation of the distance $d_{Cr\text{-}Cr}$ 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 [1].

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 θ_p of a large varieties of spinel shows a remarkable sensitivity to the nature of the A-site cation[18].

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 ferromagneticly. For x = 0.45, the situation is

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 satisfies[20]. 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 very sensitive to the strength of results obtained using simplifying assumption is doubtful.

Concerning the critical exponents β, δ and γ, 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 [23].

The values of δ 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:

$$E(\mathbf{k}) = [F(\mathbf{0}) - F(\mathbf{k})] \qquad (1A)$$

where $F(\mathbf{k}) = \frac{1}{N}\sum_{i,j} J_{ij}\, exp(i\,\mathbf{k}.\mathbf{R}_{ij})$ 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 :

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

We note that in a cubic lattice, the dispersion relation is isotropic and has the quadratic form $E(\mathbf{k}) = D\mathbf{k}^2$, where D is called the spin-wave stiffness coefficient. However the relation 2A is not isotropic, consequently the expression of B would be different.

The thermal variation of the zero temperature magnetization is due to the low temperature spin-wave excitations (magnons) which we consider without interaction, the expression is given by:

$$M(T) = M(0) - \frac{g\mu_B V}{8\pi^3}\int \frac{d^3k}{exp(\frac{E(\mathbf{k})}{k_B T}) - 1} \qquad (3A)$$

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

The volume $V = \frac{Na^3}{Q}$, 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 :

$$M(T) = M(0)\left[1 - BT^{\frac{3}{2}}\right] \qquad (4A)$$

Where:

$$B = \frac{1.87}{QS}\left(\frac{k_B}{2S(J_1+10J_2+12J_3)}\right)^{3/2} \frac{1}{\left\{1 - \frac{48(J_2+J_3)^2}{(J_1+10J_2+12J_3)^2} - \frac{128(J_2+J_3)^3}{(J_1+10J_2+12J_3)^3}\right\}^{1/2}} \qquad (5A)$$

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

[1] E. Agostinelli, C. Bahistoni, D. Fiorani, G. Mahogno and M. Nogues, J. Phys. Chem. Sol. 50, 269 (1989).
[2] M. Nogues, J. L. Dormann, J. Magn. Magn. Mat. 87, 54 (1986).
[3] M. Hamedoun, A. Zerhouni, A. Rachadi, M. Slimani and A. Benyoussef, Phys. Stat. Sol.(b) 192, 159 (1995).
M. Hamedoun, A. Hourmatallah, A. Zerhouni, N. Benzakour, A. Belayachi and M. Nogues, Phys. Stat. Sol.(b) 203, 521 (1997).
[4] P. K. Baltzer, H. W. Lehmann and M. Robbins, Phy. Rev. Lett. 15, 493 (1965).
[5] F. K. Lotgering, Philips Rev. Rep. 11, 190 (1956).
[6] R. Plumier, J. Phys. 27, 213 (1966).

[7] H. E. Stanley, Introduction to Phase Transition and Critical Phenomena (Oxford University Press, Oxford, 1971)
[8] M. E. Fisher, Rev. Mod. Phys. 46, 597 (1974).
[9] J. L. Dormann, A. Belayachi and M. Nogues, J. Magn. Magn. Mat. 104, 239 (1992).
[10] K. M. Lee and M. J. O'Shea, J. Appl. Phys. 67, 5781 (1990).
[11] C. Domb and D. L. Hunter, Proc. Phys. Soc. London 86, 1147 (1965).
[12] L. P. Kadanoff, Physics 2, 263 (1966).
[13] M. Fähnle, W. -U. Kellner and H. Kronmüller, Phys. Rev. B 35, 3640 (1987).
[14] W. E. Holland and H. A. Brown, Phy. Stat. Sol. (a) 10, 249 (1972).
[15] F. K. Lotgering, Solid State Commun. 3, 347 (1965).
[16] G. Bush, B. Magyar and O. Vogt, Sol. State Commun. 7, 509 (1969).
[17] M. Hamedoun, A. Rachadi, A. Zerhouni, H. Lassri and M. Nogues, Physica B, 229, 96, (1996).
[18] P. K. Baltzer, P. J. Wojtowics, M. Robbins and E. Lopatin, Phys. Rev. 151, 367 (1966).
[19] R. Plumier, C. R. Acad. Sci. Paris 260, 3348 (1965).
[20] M. Hamedoun, A. Rachadi, A. Hourmatallah, D. Elalam and A. Benyoussef, Phy. Stat. Sol. (b) 191, 503 (1995).
[21] K. Dwight and N. Menyuk, Phys. Rev. 163, 435 (1967).
[22] For a review, see M. F. Collins, Magnetic Critical Scattering (Oxford University Press, Oxford, 1989) and references cited thereim.
[23] K. Westerholt, H. Bach and R. Romer, J. Magn. Magn. Mat. 45, 252 (1982).