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Study of magnetic and structural in $CdGa_{2-2x}Cr_{2x}Se_4$ materials

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The magnetic semiconductor $CdGa_{2-2x}Cr_{2x}Se_4$ systems with 0≤x≤1 have been grown by using the chemical vapour transport technical in a closed system. The transporting agent was $CdCl_2$ in a proportion of 0.75 mg/cc of capsule. The starting material was previously synthesized. The structural characterization on the crystals was done by powder X-ray diffraction studies. The results show three different phases for various Cr concentration ranges: spinel structure for $x \geq 0.7$, rhombohedral for $0.5 \leq x \leq 0.6$ and tetragonal for $0 \leq x \leq 0.4$. The temperature dependence of the magnetization suggests that the studied compound presents a ferromagnetic, the phase with complex spin arrangement induced by fluctuating exchange, the paramagnetic behavior and the spin-glass behaviour. The nearest neighbour $J_1(x)$ and the next-neighbour super-exchange $J_2(x)$ interactions are evaluated by using the mean field theory for the spinels $CdGa_{2-2x}Cr_{2x}Se_4$ systems in the range $0.8 \leq x \leq 1$. The magnetic exchange energy, the intraplanar and the interplanar interactions are deduced. The high-temperature series expansion (HTSE) combined with the Padé approximants method (PA) is applied to the spinels $CdGa_{2-2x}Cr_{2x}Se_4$ systems to determine the magnetic phase diagrams, i.e. T_C versus dilution *x*. The critical exponents associated with the magnetic susceptibility χ and with the correlation length ξ are deduced in the range 0.6≤x≤1.

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1. Introduction

The spinels systems, with formula AB_2X_4 are of continuing interest because of their wide variety of physical properties. This is essentially related to (i) the existence of two types of crystallographic sublattices, tetrahedral (A) and octahedral (B), available for the metal ions, (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 solid solutions of thiospinels and selenospinels have received considerable attention for their interesting electrical and magnetic properties, which can vary greatly as a function of composition [1-5]. The magnetic of the spinels $CdGa_xCr_{2-x}Se_4$ systems in the range $0 \leq x \leq 0.06$ have been studied [6]. In particular, $CdCr_2Se_4$ exhibit ferromagnetism with high magnetization and relatively high Curie temperatures $T_C = 130-142\ K$. The anisotropy caused by the Cr^{3+} host ions is found [7] to be extremely small and the resonance line very narrow.

We present in this work an study on the single crystal growth and structural characterization of the $CdGa_{2-2x}Cr_{2x}Se_4$ compounds with $0 \leq x \leq 1$. Although there are numerous data available for $CdCr_2Se_4$ compound, the studies on effect of dilution of chromium atoms by non magnetic gallium atoms are very scarce. The magnetic properties of $CdGa_{2-2x}Cr_{2x}Se_4$ have been studied.

The exchange interactions $J_1(x)$ and $J_2(x)$ of the diluted systems $CdGa_{2-2x}Cr_{2x}Se_4$ have been obtained by using the mean field theory in the range $0.8 \leq x \leq 1$, on the basis of magnetic results [8]. The values of the intra-plane and inter-plane interactions $J_{aa}(x)$, $J_{ab}(x)$ and $J_{ac}(x)$ are deduced for $0.8 \leq x \leq 1$.

Another part of this study concerns the interesting topic of magnetic structure and spin glass behaviour in the diluted spinels $CdGa_{2-2x}Cr_{2x}Se_4$ systems for $0 \le x \le 1$. The Padé approximant (PA) [9] analysis of the high-temperature series expansion (HTSE) has been shown to be a useful method for the study of the critical region [10,11]. We have used this method to determine the critical temperatures and the critical exponents associated with the magnetic susceptibility and with the correlation length in the range $0.6 \le x \le 1$.

2. Experiment

Single crystals of the spinels $CdGa_{2-2x}Cr_{2x}Se_4$ systems for $0 \le x \le 1$ were grown by the chemical transport technical [8] in closed quartz capsules. The starting materials for the growing process were polycrystalline compounds, previously synthesized from pure elements with $4N$ or $5N$ as purity. The stoichiometric mixtures of the elements were sealed in evacuated quartz capsules (11 cm long and 9 mm as internal diameter). The capsules were slowly heated by means of an automatic temperature controller, from RT to 925 °C over a period of 10-15 days, depending upon the chromium concentration. The previously synthesized material, about 1.4 gr, was sealed in a large quartz ampoule: 20 cm long and 20 mm in inner diameter under vacuum of 10^{-5} Torr. I_2, $CrCl_3$ or $CdCl_2$ compounds were used as transport agent, in a concentration of about 0.75 mg/cc of ampoule in the case of $CdCl_2$ and 0.5 mg/cc for the iodine. The selected amount of agent depend on the chromium concentration, thus I_2 was used for the low concentration Cr sample and $CrCl_3$ was used in sample with $x = 0.8$. The ampoules were placed in a closed horizontal two zone furnace. The furnace temperature was raised over a 9 hour period to 700 °C in the charge zone and 800°C in the deposition zone. After one day the temperature gradient was inverted, in a period of 4 hrs, to get the working gradient [8].

X-ray powder diffraction studies were carried out with a Siemens D5005 diffractometer equipped with $CuK\alpha$ radiation tube ($\lambda = 1.54059$ Å, 40 Kv and 30 mA), in a $\frac{2\theta}{\theta}$ configuration. The 2θ range was $10-100^{\circ}$ with a step with of 0.02° and integration time 35 s. The magnetization was measured in the range $\cong 5K-300K$ under applied fields up to $H = 500Oe$.

3. Results

The X-ray powder diffraction studies of the samples showed that the obtained single crystals present different crystal structures for different chromium concentrations ranges, thus for $0 \le x \le 0.4$ the samples crystallises in tetragonal structure, for samples with $0.5 \le x \le 0.6$ the structure is rhombohedral and a spinel structure appears for samples with $0.7 \le x \le 1$. The magnetic experiments were performed with a Squid magnetometer in the range of 5-300 K and under the field $H = 500Oe$ by measuring the temperature dependence of the magnetization and the magnetic susceptibility for $0.1 \le x \le 0.8$ (see Ref [8])

Figs 1 and 2, shows the temperature dependence of the magnetization and the inverse of the magnetic susceptibility for $CdGa_{0.4}Cr_{1.6}Se_4$ system for a magnetic field of $500Oe$, respectively [8]. The saturation magnetization M_s (M(T=0) decreases when one decreases the dilution x (see Figs 1 and 3).

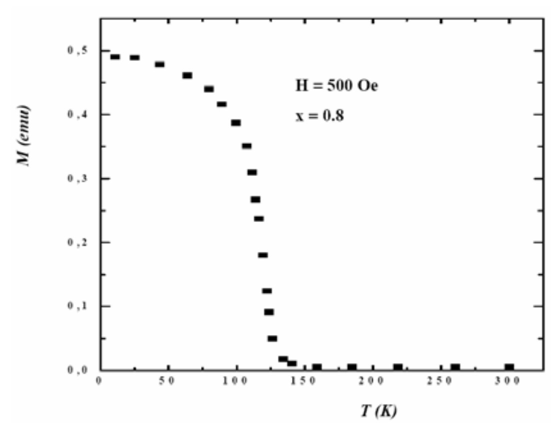

Fig 1. Temperature dependence of the magnetization at low field $(H = 500Oe)$ for the $CdGa_{2-2x}Cr_{2x}Se_4$ $(x = 0.8)$.

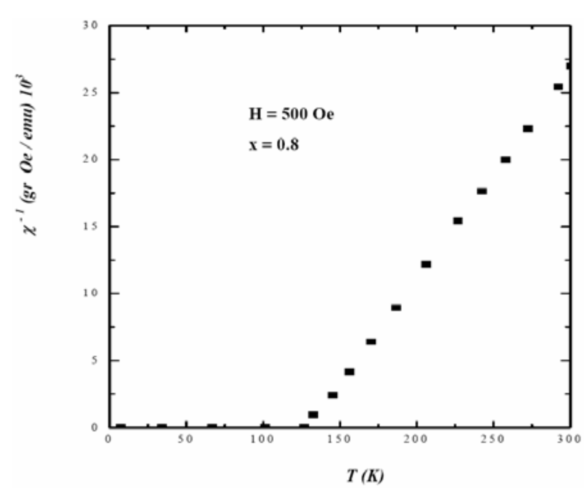

Fig 2. Temperature dependence of the inverse of the magnetic susceptibility at low field $(H = 500Oe)$ for the $CdGa_{2-2x}Cr_{2x}Se_4$ $(x = 0.8)$.

4. Theoretical method (this method is more retailed in the Ref [6])

4.1 Calculation of the values of the exchange integrals from mean field approximation

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

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

where, J_{ij} is the exchange integral between the spins situated at sites *i* and *j*. $\vec{S}_i$ is the spin operator of the spin localised at the site *i*. In this work we consider the nearest neighbouring (*nn*) and next-nearest neighbouring (*nnn*) interactions J_1 and J_2, respectively. Following, the method of Holland and Brown [12], the expressions of T_C and θ_p describing the systems $CdGa_{2-2x}Cr_{2x}Se_4$ are given in Ref [6]:

Using the experimental values of T_C and θ_p obtained by magnetic measurement [8] and [13], the values of exchange integrals $J_1(x)$ and $J_2(x)$ in the ordered phase (FM) have been evaluated (see Table 1). The corresponding magnetic exchange energy is given by using the expression given in Ref [14]. The obtained values of the intra-plane, inter-plane interactions, the ratio of inter to intraplanar interactions $\frac{J_{inter}}{J_{intra}} = \frac{(J_{ab}+J_{ac})}{J_{aa}}$ [15] and the exchange energy for the magnetic structure [16] are given in table 1 for $0.8 \le x \le 1$. The value obtained of $J_1(x)$ and $J_2(x)$ will be used in the subsection 4(b).

4.2 High-temperature Series Expansions

In this section we have used the results given by the high-temperature series expansions (HTSE) for both the zero field magnetic susceptibility $\chi(T)$ and the correlation length $\xi(T)$ with arbitrary $y = \frac{J_2}{J_1}$ up to sixth order $\beta = \frac{1}{k_B}$ (k_B is the Boltzmann's constant) in Ref [16]:

The simplest assumption that one can make concerning the nature of the singularity of the magnetic susceptibility $\chi(T)$ and the correlation length $\xi(T)$ are that at the neighbour hood of the critical point the above two functions exhibit an asymptotic behaviour:

$$\chi(T) \propto (T - T_C)^{-\gamma} \quad (2)$$

$$\xi^2(T) \propto (T_C - T)^{-2\nu} \quad (3)$$

Estimates of T_C, γ and ν for $CdGa_{2-2x}Cr_{2x}Se_4$ have been obtained using the Padé approximate method (P.A) [9] in the range $0.6 \le x \le 1$. The simple pole corresponds to T_C and the residues to the critical exponents γ and ν.

5. Discussion

The X-ray powder diffraction studies of the samples showed that the obtained single crystals present different crystal structures for different chromium concentrations ranges, thus for $0 \le x \le 0.4$ the samples crystallises in tetragonal structure, for samples with $0.5 \le x \le 0.6$ the structure is rhombohedral and a spinel structure appears for samples with $0.7 \le x \le 1$. The changes of magnetic ions favour the structural changes. The magnetic measurements of the systems $CdGa_{2-2x}Cr_{2x}Se_4$ with x = 0.8, 0.3 and 0.2 are given (see Figs 1, 2 and 3). As seen from the $M-T$ curve, M increases with decreasing temperature, and then increases abruptly neat T_C due to the paramagnetic-ferromagnetic (PM-FM) transition (see Fig. 1). The Curie temperature, defined as the temperature corresponding to a maximum of magnetic susceptibility gives $T_C = 129.4K$. The temperature dependence of the inverse susceptibility $\chi^{-1}(T)$ (Fig 2) showed a clear deviation of the Curie-Weiss law behavior in the region, closed to the transition PM-FM above $128.4K$

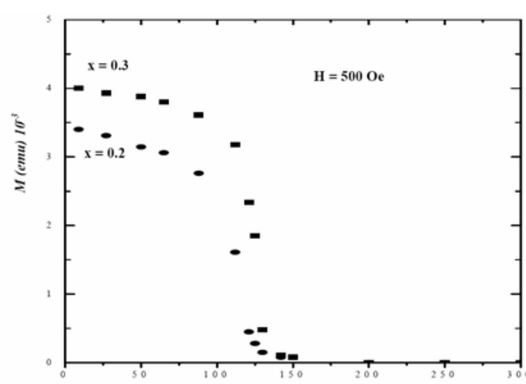

Fig. 3. Temperature dependence of the magnetization at low field $(H = 500Oe)$ for the $CdGa_{2-2x}Cr_{2x}Se_4$ $(x = 0.3, 0.2)$.

On the author hand, the nearest neighbour $J_1(x)$ and the next-neighbour super-exchange $J_2(x)$ interactions are deduced by using the experimental values of T_C and θ_p given in Refs [8, 13]. By using the value obtained of $J_1(x)$ and $J_2(x)$, we have deduced the values of the intra-plane (J_{aa}, J_{bb}), the inter-plane (J_{ac}) interactions, the energy of the magnetic structure and the ratio of inter to intraplanar interactions $\frac{J_{inter}}{J_{intra}}$ for the spinels $CdGa_{2-2x}Cr_{2x}Se_4$ systems in the range $0.8 \le x \le 1$. The obtained values are given in Table 1.

Table 1. The critical temperature $T_C(K)$, the Curie-Weiss temperature $\theta_p(K)$, the values of the first, second, intra-plane and inter-plane exchange interactions, the ratio of inter to intraplanar interactions $\frac{J_{inter}}{J_{intra}} = \frac{(J_{ab}+J_{ac})}{J_{aa}}$ and the energy of the magnetic structure of $CdGa_{2-2x}Cr_{2x}Se_4$ as a function of dilution x.

x	$T_C(K)$	$\theta_P(K)$	$\frac{J_1}{k_B}(K)$	$\frac{J_2}{k_B}(K)$	$\frac{J_{aa}}{k_B}(K)$	$\frac{J_{ab}}{k_B}(K)$	$\frac{J_{ac}}{k_B}(K)$	$\frac{(J_{ab}+J_{ac})}{J_{aa}}$	$\frac{\lvert E\rvert}{k_B S^2}(K)$
1	129.8 [8]	204.0 [8]	19.780	-3.090	39.560	54.40	-12.36	1.062	183.600
	129 [13]	166.2 [13]	22.12 [13] 18.44	-1.84 [13] -3.68	- 36.88	- 44.32	- -14.72	- 0.80	- 66.48
0.8	129.4 [13]	128.4 [13]	16.220	-3.831	32.440	34.232	- 15.324	0.582	115.533
	125.8 [13]	178.4 [13]	21.84 [13] 18.52	-1.66 [13] -1.92	- 37.04	- 58.72	- -7.68	- 1.377	- 88.08

The high-temperature series expansions (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 range $0.6 \le x \le 1$ (see Table 1.). The value of critical exponents associated with the magnetic susceptibility and with the correlation length γ and ν, respectively, have been estimated in the range of the composition $0.8 \le x \le 1$. 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 central critical exponents are found to be $\gamma = 1.380 \pm 0.004$ and $\nu = 0.71 \pm 0.01$, respectively.

6. Conclusions

The different structures of $CdGa_{2-2x}Cr_{2x}Se_4$ have been studied by using the X-ray diffraction. The magnetic properties of this system are studied. The exchange interactions are obtained by mean field theory. The sign of the first and super-exchange interactions are positives and negatives, respectively, and decreases with x decreases in the range $0.8 \le x \le 1$. These results are comparable with those given by Ref [17] (see Table 1). The same variation notices for the J_{aa}, J_{bb} and J_{ac} interactions and the energy of the magnetic structure (see table 1). The obtained value of the ratio of inter to intraplanar interactions decreases when x decreases. This variation is responsible to describing the collinear isotropic magnetic structures for the range $0.8 \le x \le 1$. The HTSE is applied to find the magnetic critical temperature of the $CdGa_{2-2x}Cr_{2x}Se_4$ systems(see Table 1). The theoretical and the experimental results obtained are comparable in the range $0.8 \le x \le 1$. The value of critical exponents associated with the magnetic susceptibility and with the correlation length γ and ν, respectively, are obtained and nearest of Heisenberg model [18].

References

[1] M. Hamedoun, M. Houssa, N. Benzakour, A. Hourmatallah, J. Phys: Condens. Matter. **10,** 3611 (1998).

[2] M. Hamedoun, M. Houssa, N. Benzakour, A. Hourmatallah, Physica B. **270**, 384 (1999) -390.

[3] Y. Cherriet, M. Hamedoun, J. Magn. Magn. Mater. **224** (2001) 106-112; F. Mahjoubi, M. Hamedoun, F.Z. Bakkali, A. Hourmatallah, A. Benyoussef, J. Magn. Magn. Mater. **221** (2000) 359.

[4] A. I. Abramovich, L. I. Koreleva, L. N. Lukina, Phys. Solid State. **41** (1999) 73.

[5] A. Rachadi, M. Hamedoun, D. Allam, Physica B. **222** (1996) 160.

[6] H. Bakrim, K. Bouslykhane, M. Hamedoun, A. Hourmatallah, N. Benzakour, J. Magn. Magn. Mater. **285** (2005) 327-334

[7] R. C. LeCraw, H. von Phylipsborn, and M. D. Sturge, J. Appl. Phys. **38** (1967) 965.

[8] M.L. Leticia. de Chalbaud, V.Sagredo, Alfa Meeting-Viena-Austria, April. (2004).

[9] "Padé Approximants", edited by G. A. Baker and P. Graves-Morris (Addison-Wesley, London, 1981).

[10] R. Navaro, Magnetic Properties of Layered Transition Metal Compounds, Ed. L.J.DE Jonsgh, Daventa: Kluwer 1990 (p.**105**).

[11] M. C. Moron, J. Phys: Condensed Matter. **8** (1996) 11141.

[12] W. E. Holland and H. A. Brown, Phys. Stat. Sol (a). **10** (1972) 249.

[13] T. Groń, A. Krajewski, J. Kusz, E. Malicka, I. Okońska-Kozlowska, A. Waśkowska, Phys. Rev B. **71** (2005) 035208.

[14] M. Hamedoun, A. Wiedenmann, J. L. Dormann. M. Nogues, J. Rossat-Mignod, J. Phys. C : Solid State Phys. **19** (1986) 1783-1800; M. Hamedoun, Dr. thesis, Faculty of Orsay, France, (1984).

[15] M. Hamedoun, A. Rachadi, A. Hourmatallah, D. El Allam, A. Benyoussef, Phys. Stat. Sol. (b). **191** (1995) 503.

[16] N. Benzakour M. Hamedoun, M. Houssa, A. Hourmatallah, and F. Mahjoubi, Phys. Stat. Sol. (b). **212** (1999) 335.

[17] M. Hamedoun, R. Masrour, K. Bouslykhane, A. Hourmatallah, N. Benzakour, Chin. Phys. Lett. **24** (2007) 7.

[18] M. F. Collins, Magnetic Critical Scattering, Oxford University Press, Oxford 1989, and references cited therein.

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