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Review

Magnetic properties of the spinel systems ACr_2X_4 (A = Zn, Cd, Hg; X = S, Se)

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ABSTRACT

The magnetic properties of the spinels systems $Zn_{1-x}Cd_xCr_2Se_4$ and $Hg_{1-x}Cd_xCr_2S_4$ have been studied by mean-field theory and high-temperature series expansions in the range $0 \le x \le 1$. The nearest neighbour and the next-nearest-neighbour super-exchange interaction $J_1(x)$ and $J_2(x)$ respectively, are calculated for the two systems, using the first theory in the range $0 \le x \le 1$. The intra-planar and the inter-planar interactions are deduced. The corresponding classical exchange energy for the magnetic structures is obtained.

The second theory has been applied to the spinel systems $Zn_{1-x}Cd_xCr_2Se_4$ and $Hg_{1-x}Cd_xCr_2S_4$, combined with the Padé approximants method, to determine the magnetic phase diagrams (T_C versus dilution x) in the range $0 \le x \le 1$. The obtained theoretical results are in agreement with the experimental ones obtained by magnetic measurements. The critical exponents associated with the magnetic susceptibility (γ) and with the correlation lengths (ν) are deduced for the two systems in the ordered phase.

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1. Introduction

During the last decade the fascinating physics of spinel compounds came into the focus of modern solid-state physics and materials science. Materials with spinel structures, with the 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 over the two sublattices, with a large possibility of reciprocal substitution between them. Solid solutions of thiospinels and selenospinels have received considerable attention because of their interesting electrical and magnetic properties, which can vary greatly as a function of composition [1–7]. The compounds $HgCr_2S_4$, $CdCr_2S_4$, $HgCr_2Se_4$ and $CdCr_2Se_4$ are known to be ferromagnetic spinels [8–11], whereas $ZnCr_2S_4$ and $ZnCr_2Se_4$ are known to be antiferromagnetic [12,13]. The chromium ion Cr^{3+} occupies the octahedral sites in the spinel B sublattice and the Cd^{2+} occupies the tetrahedrally coordinated A sublattice. In the mixed spinels $Zn_{1-x}Cd_xCr_2Se_4$ and $Hg_{1-x}Cd_xCr_2S_4$, two important frustration effects are present: the topological frustration in presence of antiferromagnetic interactions and the competition between n.n. ferromagnetic Cr–Se(S)–Cr interactions J_1 and high-order-neighbours antiferromagnetic Cr–Se(S)–(Zn, Cd, Hg)–Se(S)–Cr interactions J_2. Zn, Hg and Cd are involved as an intermediate in super-exchange interactions between higher-order neighbours.

In this work, the first- and the second-nearest-neighbours exchange interactions $J_1(x)$ and $J_2(x)$ are calculated on the basis of magnetic-measurement results in $Zn_{1-x}Cd_xCr_2Se_4$ and

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Table 1

The critical temperature $T_C(K)$, the Néel temperature $T_N(K)$, the Curie–Weiss temperature θ_p, values of the first, second, intra-plane, inter-plane exchange integrals, the ratio of inter- to-intra-planar and the energy of $Zn_{1-x}Cd_xCr_2Se_4$ as a function of dilution x.

x	T_N (K) [14]	T_C(K) [14]	θ_p (K) [14]	J_1/kB (K)	J_2/kB (K)	J_{aa}/kB (K)	J_{ab}/kB(K)	J_{ac}/kB (K)	$\lvert(J_{ab}+J_{ac})/J_{aa}\rvert$	E/kBS^2 (K)
1.0	–	130.00	204.00	19.800	−3.100	39.600	54.400	−12.400	1.060	81.600
0.8	–	103.50	195.13	16.854	−1.922	33.708	52.040	−7.688	1.315	78.060
0.6	–	72.60	174.30	13.070	−0.725	26.140	46.480	−2.900	1.667	69.720

$Hg_{1-x}Cd_xCr_2S_4$ in the range $0 \le x \le 1$ [14]. The values of the intra-plane and inter-plane interactions J_{aa}, J_{ab} and J_{ac}, respectively, are deduced. The interaction energy of the magnetic structure for the two systems is obtained, using the values of $J_1(x)$ and $J_2(x)$ obtained in the range $0 \le x \le 1$.

In recent work [1,2], 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 compound $ZnCr_{2x}Al_{2-2x}S_4$.

The Padé approximant (P.A.) [15] analysis of the HTSE of the correlation length has been shown to be a useful method for the study of the critical region [16–19]. The model that we used in the present work is valid in the case of a spinel structure. We have used the HTSE technique to determine the critical temperature T_C or the Néel temperature T_N and the critical exponent γ and ν associated with the magnetic susceptibility χ and with correlation length ξ, respectively, in the ordered phase.

2. Theoretical method

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

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

where J_{ij} is the exchange integral between the spins situated at sites i and j. $\vec{S}_i$ is the atomic spin of the magnetic ion located on the ith site. The factor "2" in Eq. (1) arises from the fact that, when summing over all possible pairs $\langle ij\rangle$ exchange interactions, we count each pair twice. The mean-field approximation leads to simple relations between the paramagnetic Curie-temperature θ_P and the critical temperature T_C and the two considered exchange integrals J_1 and J_2.

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; respectively, and the two exchange integrals J_1 and J_2: these can be used to derive numerical values for the exchange constants. Following the method of Holland and Brown [20], the expression of T_C and θ_P that can describe the systems $Zn_{1-x}Cd_xCr_2Se_4$ and $Hg_{1-x}Cd_xCr_2S_4$ are:

$$T_C = \frac{2S(S+1)}{3kB}[2J_1 - 4J_2] \tag{2}$$

$$\theta_P = \frac{2S(S+1)}{3kB}[6J_1 + 12J_2] \tag{3}$$

where kB is the Boltzmann constant and $S_{Cr} = 3/2$.

In the antiferromagnetic region, the Néel temperature T_N is given by [21]:

$$T_N = \frac{5}{2kB}\lambda(\varphi) \tag{4}$$

where $\lambda(\varphi)$ is the eigenvalue of the matrix formed by the Fourier transform of the exchange integral. Using Eqs. (2)–(4) together with the experimental values of T_C, T_N and θ_p [14], the values of $J_1(x)$ and $J_2(x)$ have been determined for each composition of the system. The optimum values are given in Tables 1 and 2. In the same tables we give also the values of the intra-plane and inter-plane interactions $J_{aa} = 2J_1$; $J_{ab} = 4J_1 + 8J_2$ and $J_{ac} = 4J_2$; respectively and the ratio of inter- to intra-planar interactions $J_{inter}/J_{intra} = |(J_{ab} + J_{ac})/J_{aa}|$ for $0 \le x \le 1$. The obtained values of the exchange integrals (J_1 and J_2) will be used in the following section.

The values of the corresponding classical exchange energy $E/k\mathrm{B}S^2 = 6J_1 + 12J_2$ [21] for the magnetic structure are given.

3. High-temperature series expansions

In this section we have used the results given by the HTSE for both the zero field magnetic susceptibility χ and the correlation length $\xi(T)$ with arbitrary $y = J_2/J_1$ up to sixth order β in Ref [22].

Figs. 1 and 2, show magnetic phase diagrams of $Zn_{1-x}Cd_xCr_2Se_4$ and $Hg_{1-x}Cd_xCr_2S_4$ systems, respectively. We can see the good agreement between the magnetic phase diagrams obtained by the HTSE technique and the experimental ones [23–26].

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

$$\chi(T) \propto (T - T_C)^{-\gamma} \tag{3'}$$

$$\xi^2(T) \propto (T_C - T)^{-2\nu} \tag{4'}$$

Estimates of T_C or T_N, γ and ν for $Zn_{1-x}Cd_xCr_2Se_4$ and $Hg_{1-x}Cd_xCr_2S_4$ have been obtained using the Padé approximate method (P.A.) [15]. The [M, N] PA to the series $F(\beta)$ is a rational fraction P_M/Q_N, with P_M and Q_N, polynomials of degree M and N in $\beta = 1/k\mathrm{B}T$, satisfying: $F(\beta) = P_M/Q_N + O(\beta^{M+N+1})$. The sequence of [$M$, N] P.A. to be both $\log(\chi(T))$ and $\log(\xi^2(T))$ are found to be convergent. The simple pole corresponds to T_C or T_N and the residues to the critical exponents γ and ν.

4. Discussions and conclusions

$J_1(x)$ and $J_2(x)$ have been determined from mean-field theory, using the experimental data of T_C or T_N and θ_p [14] for each

Table 2

The critical temperature T_C (K), the Néel temperature T_N (K), the Curie–Weiss temperature θ_p, values of the first, second, intra-plane, inter-plane exchange integrals, the ratio of inter- to-intra-planar and the energy of $Hg_{1-x}Cd_xCr_2S_4$ as a function of dilution x.

x	T_N (K) [14]	T_C (K) [14]	θ_p (K) [14]	J_1/kB (K)	J_2/kB (K)	J_{aa}/kB (K)	J_{ab}/kB (K)	J_{ac}/kB (K)	$\lvert(J_{ab}+J_{ac})/J_{aa}\rvert$	E/kBS^2 (K)
1.0	–	84.00	152.78	13.492	−1.653	26.984	40.744	−6.612	1.246	61.116
0.6	–	71.32	159.86	12.46	−0.901	24.920	42.632	−3.604	1.566	63.948
0.4	–	61.88	158.68	11.477	−0.449	22.954	42.316	−1.796	1.765	63.474

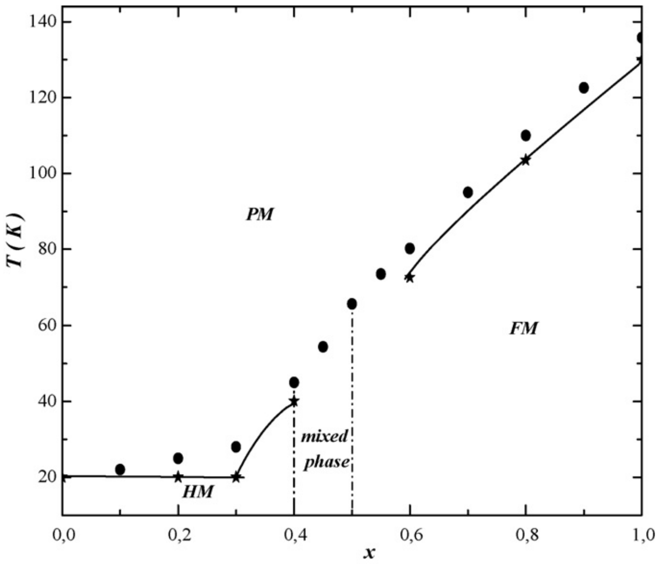

Fig. 1. Magnetic phase diagram of $Zn_{1-x}Cd_xCr_2Se_4$. The various phases are the paramagnetic phase (PM), ferromagnetic phase (FM) $(0.5 \leq x \leq 1)$, mixed phase $(0.4 \leq x < 0.5)$ and helimagnetic (HM) $(0 \leq x < 0.4)$. The solid circles are the present results (given by HTSE method). The solid star represents the experimental points deduced by magnetic measurements [14].

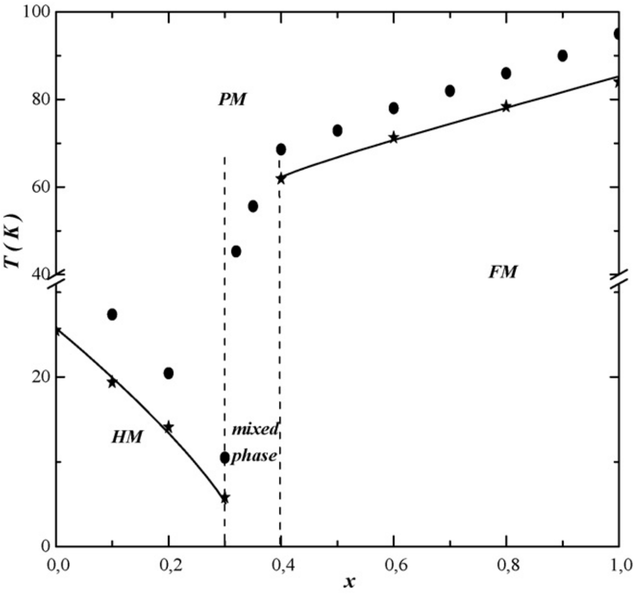

Fig. 2. Magnetic phase diagram of $Hg_{1-x}Cd_xCr_2S_4$. The various phases are the paramagnetic phase (PM), ferromagnetic phase (FM) $(0.4 \leq x < 1)$, phase mixed $(0.35 \leq x < 0.4)$, and helimagnetic (HM) phase $(0 \leq x \leq 03.5)$. The solid circles are the present results (given by HTSE method). The solid star represents the experimental points deduced by magnetic measurements [14].

dilution. From these values we have deduced the values of the intra-plane and inter-plane interactions J_{aa}, J_{bb} and J_{ac}, respectively, the energy of the magnetic structures and the ratio of inter to intra-planar interactions $J_{\text{inter}}/J_{\text{intra}} = |(J_{ab} + J_{ac})/J_{aa}|$. The values obtained for $Zn_{1-x}Cd_xCr_2Se_4$ and $Hg_{1-x}Cd_xCr_2S_4$ are given in Tables 1 and 2 in the range $0 \leq x \leq 1$.

From Table 1 corresponding to $Zn_{1-x}Cd_xCr_2Se_4$, on can see that $J_1(x)$ and the absolute value of $J_2(x)$ decreases with x. The decrease in $J_1(x)$ is due to the change in the average value of the Cr–Cr distance. $J_2(x)$ represents the strength of the Cr–Se–A–Se–Cr super-exchange, we expect its value to depend on the nature of the A-site cation. The ratio $J_{\text{inter}}/J_{\text{intra}} = |(J_{ab} + J_{ac})/J_{aa}|$ increases when x decreases. This variation is responsible on the apparition of the magnetic spiral structure (HM) in $ZnCr_2Se_4$.

From Table 2 corresponding to $Hg_{1-x}Cd_xCr_2S_4$, the situation is different. $J_1(x)$, $J_2(x)$ and the exchange energy decrease in absolute value with deceases x. It is found that the intra-plane interaction J_{aa} at high concentrations of Cadmium, but the inter-plane interaction appears and reduces the stabilization of ferromagnetism at sufficiently low concentrations.

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 or T_N for each dilution x. The obtained magnetic phase diagrams of the $Zn_{1-x}Cd_xCr_2Se_4$ and $Hg_{1-x}Cd_xCr_2S_4$ systems are presented in Figs. 1 and 2, respectively. Several thermodynamic phases may appear including the paramagnetic (PM), ferromagnetic (FM) $0.5 \leq x \leq 1$ for $Zn_{1-x}Cd_xCr_2Se_4$ $(0.4 \leq x < 1$ for $Hg_{1-x}Cd_xCr_2S_4)$, mixed phases for $Zn_{1-x}Cd_xCr_2Se_4$ $(0.4 \leq x < 0.5)$ and for $Hg_{1-x}Cd_xCr_2S_4)$ in $0.35 \leq x < 0.4$, helimagnetic (HM) in $0 \leq x \leq 03.5$ for $Hg_{1-x}Cd_xCr_2S_4$ and in $0 \leq x \leq 0.4$ for $Zn_{1-x}Cd_xCr_2Se_4$. In these figures we have included, for comparison, the experimental results obtained by magnetic measurement. From these figures one can see good agreement between the theoretical phase diagram and experimental results. In addition, we have determined the region spin glass while using the expression of the nonlinear susceptibility. In the other hand, the value of critical exponents γ and ν associated with the magnetic susceptibility $\chi(T)$ and with the correlation length $\xi(T)$, have been estimated in the ordering phase. The sequence of $[M, N]$ PA to series of $\chi(T)$ has been evaluated. By examining the behaviour of these PA, the convergence was found to be quite rapid. Estimates central values of the critical exponents associated with the magnetic susceptibility and with the correlation length are found to be $\gamma = 1.373 \pm 0.002$, $\nu = 0.695 \pm 0.004$ and $\gamma = 1.381 \pm 0.002$, $\nu = 0.694 \pm 0.008$, for two systems $Zn_{1-x}Cd_xCr_2Se_4$ and $Hg_{1-x}Cd_xCr_2S_4$, respectively. These values are insensitive to dilution x in phase ordering for two systems. The values of γ and ν are nearest to the one of 3D Heisenberg model [27], namely, 1.3866 ± 0.0012, and 0.7054 ± 0.0011. To conclude, it would be interesting to compare the critical exponents γ 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. Zarek [28] 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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