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Magnetic phase diagram of diluted spinel $Zn_{1-x}Cu_xCr_2Se_4$ system

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Abstract

By using mean field theory, we have evaluated the nearest-neighbour and the next-neighbour super-exchange $J_1(x)$ and $J_2(x)$, respectively, for $Zn_{1-x}Cu_xCr_2Se_4$ in the range $0 \leqslant x \leqslant 1$. The intraplanar and the interplanar interactions are deduced. High-temperature series expansions are derived for the magnetic susceptibility and two-spin correlation functions for a Heisenberg ferromagnetic model on the B-spinel lattice. The calculations are developed in the framework of the random phase approximation. The magnetic phase diagram is deduced. A spin glass phase is predicted for intermediate range of concentration. The results are comparable with those obtained by magnetic measurements. The critical exponents associated with the magnetic susceptibility (γ) and the correlation lengths (ν) have been deduced. The values are comparable to those of the 3D Heisenberg model, and are insensitive to the dilution x.

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Keywords: Spinel; Exchange interaction; Critical exponent; Phase diagram

1. Introduction

Recently magnetic chalcogenides crystallising in the spinel structure have attracted considerable attention. Within the last few years exotic phenomena and fascinating ground states have been observed in this class of materials: heavy-fermion behaviour [1], complex spin order and spin dimerisation [2–4], spin–orbital liquid [5] and orbital glass [6], as well as coexistence of ferromagnetism and ferroelectricity [7,8]. They are attributed to the cooperativity and competition between charge, spin and orbital degrees of freedom, all of which are strongly coupled to the lattice. In addition, topological frustration due to the tetrahedral arrangement of the magnetic cations and bond frustration due to competing ferromagnetic (FM) and antiferromagnetic (AFM) exchange interactions hamper any simple spin and orbital arrangement in the ground state. The $Zn_{1-x}Cu_xCr_2Se_4$ is normal spinel with strong preference of Cr ions to locate in the octahedral (B) positions. Substitution of Zn with Cu ions gives a structural solid solution of the normal spinel structure [9] and causes fundamental changes of both magnetic and electrical properties. These systems are still the subject of extensive experimental and theoretical studies [10–14]. The stochiometric compounds $ZnCr_2Se_4$ ($x=0$) and $CuCr_2Se_4$ ($x=1$) are, respectively, semiconductor with a magnetic spiral structure [15,16], (with spiral angle $\varphi = 42^\circ \pm 1$) and metallic ferromagnet [16,17]. The Néel temperature of the former is $T_N = 22$ K ($x=0$), while the Curie temperature of the latter is much higher and equal to $T_C = 416$ K ($x=1$). In $ZnCr_2Se_4$, with the highest Cr–Cr ($d_{Cr-Cr} = 3.53$ Å) separation, the direct exchange is almost suppressed and the spin arrangement follows from the dominating FM nn (nearest-neighbour) 90° Cr–Se–Cr exchange and the additional AFM nnn (next nearest-neighbour) Cr–Se–Zn–Se–Cr and Cr–Se–Se–Cr exchange interactions [18].

In recent works [19], we have used the high-temperature series expansions (HTSE) to study the thermal and disorder variation of the short-range order (SRO) in the

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Table 1
The Néel temperature T_N (K), the critical temperature T_C (K), the Curie–Weiss temperature θ_p (K) given by magnetic measurement and the values of the first, second, intra-planar, inter-planar exchange integrals, the ratio of inter-to-intraplanar and the energy of the magnetic structure obtained by mean-field theory of the $Zn_{1-x}Cu_xCr_2Se_4$ system in this work

x	$T_{N,C}$ (K) [24]	θ_p (K) [24]	J_1/K_B (K)	J_2/K_B (K)	J_{aa}/K_B (K)	J_{ab}/K_B (K)	J_{ac}/K_B (K)	$\lvert(J_{ab}+J_{ac})/J_{aa}\rvert$	$E(K)/K_B(S^2)$
0.00	22	118	7.866	−2.646	15.732	10.296	−10.584	0.0183	15.444
0.01	20	142	9.466	−3.138	18.932	12.760	−12.552	0.0109	19.140
0.02	16	188	12.533	−4.090	25.065	17.412	−16.360	0.0420	26.118
0.025	10	240	16.000	−5.221	32.000	22.232	−20.884	0.0421	33.348
0.05	14	276	18.400	−5.920	36.800	26.240	−23.680	0.0695	39.360
0.07	16	296	19.733	−6.260	39.466	28.852	−25.040	0.0965	43.278
0.1	20	332	22.133	−6.839	44.266	33.820	−27.356	0.1460	50.730
0.2	377	388	50.633	−12.383	101.266	103.468	−49.532	0.5320	155.202
0.3	382	391	51.233	−12.583	102.466	104.268	−50.332	0.5260	156.402
0.5	390	396	52.200	−12.900	104.400	105.600	−51.600	0.5170	158.400
0.7	395	411	53.200	−12.900	106.400	109.600	−51.600	0.5450	164.400
0.8	404	418	54.333	−13.233	108.666	111.468	−52.932	0.5380	167.202
0.9	408	427	55.033	−13.283	110.066	113.868	−53.132	0.5518	170.802
1	416	436	56.133	−13.533	112.266	116.268	−54.132	0.5530	174.402

particular B-spinel $CdGa_{2-2x}Cr_{2x}Se_4$ compounds. Three first spin correlation functions have been calculated with the aid of a diagrammatic representation.

In this work, by using the mean field theory, we have calculated the nearest-neighbour and the next-neighbour super-exchange $J_1(x)$ (nn) and $J_2(x)$ (nnn), respectively, for $Zn_{1-x}Cu_xCr_2Se_4$ in the range $0 \leqslant x \leqslant 1$. The values of the intraplanar and interplanar interactions $J_{aa}(x)$, $J_{ab}(x)$ and $J_{ac}(x)$, respectively, are deduced from the values of $J_1(x)$ and $J_2(x)$ for $0 \leqslant x \leqslant 1$. The interaction energy of the magnetic structure is obtained in the range $0 \leqslant x \leqslant 1$. These values are given in Table 1.

The aim of the present paper is to calculate from the results of the random phase approximation (RPA) [20,21], the magnetic susceptibility and the correlation functions for a Heisenberg FM model having both nn and nnn exchange integrals $J_1(x)$ and $J_2(x)$; respectively. Our work extends by several terms the earlier classic work on this subject by lines [21]. The HTSE of the magnetic susceptibility and correlation functions is given up $\beta = 1/K_BT$. The theoretical results obtained are then used to study the paramagnetic (PM) region of the spinel $Zn_{1-x}Cu_xCr_2Se_4$ systems in the dilution range $0 \leqslant x \leqslant 1$. In order to determine the critical temperature T_C or T_N, the critical exponents γ and ν associated with the magnetic susceptibility χ and the correlation length ξ; we have applied the Padé approximate (PA) methods [22]. The results obtained are found to be in agreement with experimental ones and can be compared with other theoretical studies based on the 3D Heisenberg model.

2. Calculation of the values of the exchange integrals

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

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

where J_{ij} is the exchange integral between the spins situated at sites i and j. $\vec{S}_i$ is the operator of the spin localised at the site i. In this work, we consider the nn and nnn, J_1 and J_2, respectively:

$$H = J_1\sum_{i,j}\vec{S}_i\vec{S}_j - J_2\sum_{i,k}\vec{S}_i\vec{S}_k. \tag{2}$$

The sums over ij and ij include all (nn) and (nnn) 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 PM Curie temperature θ_p and the critical temperature T_C or the Néel temperature T_N, respectively. The angle of helices φ is deduced in the range $0 \leqslant x \leqslant 1$.

Following, the method of Holland and Brown [23], the expressions of T_C and θ_p describing the $Zn_{1-x}Cu_xCr_2Se_4$ systems are

$$T_C = \frac{5}{2K_B}[2J_1 - 4J_2], \tag{3}$$

$$\theta_p = \frac{5}{2K_B}[6J_1 + 12J_2], \tag{4}$$

where K_B is the Boltzmann constant.

In the AFM region, we have used the formula of Néel temperature T_N given in Ref. [9]:

$$T_N = \frac{2}{3}S(S+1)\lambda(\varphi), \tag{5}$$

where $\lambda(\varphi)$ is the eigenvalue of the matrix formed by the Fourier transform of the exchange integral. We have used the experimental values of T_C or T_N, ϕ and θ_p for the $Zn_{1-x}Cu_xCr_2Se_4$, given in Ref. [24], respectively, to determinate the values of exchange integrals J_1 and J_2 for each composition x. In the same table, we also give the values of the intraplanar and interplanar interactions $J_{aa} = 2J_1$, $J_{ab} = 4J_1 + 8J_2$ and $J_{ac} = 4J_2$, respectively, and the ratio of inter-to-intraplanar interactions