Effect of magnetic dilution in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($0 < x < 0.5$)

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The profound effect of magnetic dilution in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$ is demonstrated by the analysis of neutron powder diffraction and magnetic susceptibility data. All the members of the series show a defective stannite crystal structure and a random distribution of the Mn ions. The magnetic archetype system of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$ is not found to be MnGa_2Se_4 (the magnetic end member of the series with $I\bar{4}$ symmetry) but, instead, a hypothetical compound with $I\bar{4}2m$ symmetry. The distance between the Mn ions along the various magnetic superexchange pathways is not seriously affected by the degree of dilution. However, the global magnetic interaction between manganese ions is found to be significantly higher than that expected for the classical magnetic dilution of the parent MnGa_2Se_4 . A generally applicable method for the calculation of the correct Weiss temperature θ in diluted magnetic semiconductors is provided.

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I. INTRODUCTION

The combination of two or more apparently independent areas of research often leads to valuable observations. This is the case for diluted magnetic semiconductors (DMSs). Within these materials a given concentration of a magnetic element is introduced into a nonmagnetic semiconductor matrix. The interaction between the conduction and/or valence band electrons and the localized magnetic moments of the magnetic ions gives rise to an unusual combination of magnetic, electronic, and optical properties that make DMSs important subjects for both scientific investigation and potential device applications.^{1,2} Specific properties and requirements are matched by tailoring the composition through the use of solid solutions,^{3,4} though significant differences between the crystal structure of magnetic materials and a nonmagnetic host can make the two systems incompatible with each another.⁵

The degree of atomic ordering critically influences the physical properties (optical, electronic, magnetic,...) of the material.^{6,7} A precise knowledge of the distribution of the cations in the crystal lattice is, therefore, of significant importance. In most DMSs the arrangement of the magnetic atoms is random.⁸ As a consequence, many variables follow a linear dependence versus the content of the magnetic cations, as is the case of the Weiss temperature.⁹ One of the problems encountered in DMSs is that most of these systems, particularly pseudobinary DMSs, exhibit comparatively higher θ values.¹⁰ This makes the calculation of reliable Weiss temperatures more difficult due to experimental limitations on the available temperature range.

Mn^{2+} is a magnetic ion with spin $S=5/2$. ZnGa_2Se_4 and

MnGa_2Se_4 are semiconductors showing direct gaps of around 2.3 and 2.5 eV, respectively.^{11,12} The controlled substitution of Zn ions by Mn in ZnGa_2Se_4 generates the series of DMSs $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$. Since the crystal structure of both end members of the family are rather similar (defective stannite for ZnGa_2Se_4 and defective chalcopyrite for MnGa_2Se_4), a high degree of miscibility is expected. Moreover, MnGa_2Se_4 exhibits a totally ordered scheme of the magnetic cations while ZnGa_2Se_4 shows a completely disordered arrangement of the Zn atoms.^{13,14} Interesting behavior is then expected within this series due to the competition of both order and disorder trends. From the magnetic point of view, relatively low Weiss temperature values can be anticipated since MnGa_2Se_4 orders magnetically below 6.4 ± 0.1 K.¹⁵

The aim of this research is to explore the influence of the distribution of the Mn ions on the magnetic behavior of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$, which is shown to differ significantly from that expected for the classical dilution of a magnetic semiconductor. Thus, we analyze the dependence of the magnetic superexchange constants with magnetic dilution and the magnetic archetype system corresponding to this series. The combination of neutron powder diffraction experiments and magnetic susceptibility measurements is shown to be a useful tool for the determination of correct Weiss temperatures θ in DMSs.

II. EXPERIMENT

Orange single crystals of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $x=0.00$, 0.104(4), 0.240(4), 0.343(4), and 0.482(4) were synthesized using the chemical vapor transport method.^{16,17} The Mn concentration x was obtained from powder diffraction and magnetic experiments (see Sec. III for details). The obtained values from both methods are in good agreement within the

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FIG. 1. Room-temperature unit cells of tetragonal MnGa_2Se_4 (space group $I\bar{4}$) and ZnGa_2Se_4 (space group $I\bar{4}2m$), respectively. Vac refers to a vacancy.

experimental error. No significant difference has been detected between the real and nominal values of such concentration (based on the quantity of Mn used during the synthesis).

In order to determine the distribution of magnetic ions in the samples under study, neutron diffraction experiments are considered more suitable than the more common x -ray technique. Mn is more clearly differentiated from other elements using neutrons due to its negative coherent nuclear scattering length. Room-temperature time-of-flight neutron-diffraction experiments were performed on the Polaris powder diffractometer¹⁸ at the ISIS source, UK. Thin-walled vanadium cans acted as sample containers. Diffraction data were collected in all available detector banks over a d -spacing range $0.5 < d(\text{\AA}) < 12.0$. Normalization of the data and correction for sample absorption were carried out using the GENIE software.¹⁹ The program TF14LS, based on the CAMBRIDGE CRYSTALLOGRAPHIC SUBROUTINE LIBRARY,²⁰ was used for Rietveld analysis of the diffraction patterns. Refinements of the crystal structure were carried out using the data in the range $0.8 < d(\text{\AA}) < 3.2$ obtained using the highest-resolution backscattering detectors, which possess an essentially constant resolution of $\Delta d/d \approx 5 \times 10^{-3}$.

DC magnetic susceptibility measurements were performed on a magnetometer with superconducting quantum interference device (SQUID) detection manufactured by Quantum Design. The data were collected using polycrystalline samples under an external magnetic field of 1 T. The temperature was varied between 5 and 300 K.

III. RESULTS AND DISCUSSION

A. Structure

The crystal structures of both ZnGa_2Se_4 and MnGa_2Se_4 were used as the starting models for the determination of the structural arrangement of atoms within $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$. ZnGa_2Se_4 crystallizes in the tetragonal space group $I\bar{4}2m$ possessing a defective stannite structure¹⁴ with $a = 5.511\,7(3)$ Å and $c = 10.964\,3(6)$ Å (see Fig. 1). The cations are surrounded by a tetrahedral environment of four Se atoms, with the anions located at the crystallographic positions $8i$ (x, x, z) with $x \sim 1/4$ and $z \sim 1/8$. Half of the Ga

cations occupy the $2a$ (0, 0, 0) site, while the rest share the $4d$ position [(0, 1/2, 1/4), (0, 1/2, 3/4)] with the Zn atoms. Thus, the crystal structure exhibits a random disorder comprising all the Zn and half of the Ga atoms. The structure is defective in the sense that there are some vacancies which are ordered and located at the $2b$ (0, 0, 1/2) sites.

The other end member of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series is MnGa_2Se_4 . The crystal structure of this magnetic material is rather similar to that reported for the Zn analog (see Fig. 1). The structural arrangement of the atoms corresponds to a defective chalcopyrite structure, tetragonal space group $I\bar{4}$, with $a = 5.677(1)$ Å and $c = 10.761(2)$ Å.¹³ The key difference between the crystal structure of the two end members of the series is the absence of cation disorder in MnGa_2Se_4 . Thus, the Mn atoms are located in $2d$ (0, 1/2, 3/4) crystallographic positions and half of the Ga cations are in $2c$ sites (0, 1/2, 1/4). This forces the Se anions to move into a general position $8g$, such that the x and y coordinates are no longer equal. The remainder of the Ga cations and the vacancies occupy the $2a$ (0, 0, 0) and $2b$ (0, 0, 1/2) lattice sites, respectively.

The results of the refinements of the crystal structure of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 \leq x < 0.5$ obtained using the Rietveld method are shown in Table I (see also Figs. 2 and 3). The central issue is the arrangement of the magnetic cations, which could be randomly distributed (as for the Zn ions in ZnGa_2Se_4) or ordered (as in MnGa_2Se_4). The neutron powder diffraction data show that all the materials under study retain the symmetry of the Zn derivative. Thus all of them crystallize in the space group $I\bar{4}2m$. While the reflection conditions for space groups $I\bar{4}$ and $I\bar{4}2m$ are the same, the x and y coordinates of the Se atom can be used when choosing between these space groups, since they are different for $I\bar{4}$, but equal for $I\bar{4}2m$. The refinements performed on the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 \leq x < 0.5$ series using $I\bar{4}$ symmetry give identical values for the x and y coordinates of the selenium atom within the experimental error.

The defective stannite and chalcopyrite structural arrangements can be derived from the well-known cubic zinc-blende structure by considering two different cations rather than one, introducing vacancies into the lattice, and doubling the unit-cell parameter c . This lowering of symmetry is accompanied by a relaxation of the anions with respect to the ideal zinc-blende positions at (1/4, 1/4, 1/8), etc. Considering the unit-cell dimensions, the evolution of the tetragonal parameters a and c with x is dissimilar in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 \leq x < 0.5$. While a increases with the Mn content, c remains essentially constant (see Table I). Interestingly, the decrease of c/a with x suggests a tendency to an increase in cation ordering as the Mn content increases.²¹ Moreover, the decrease of c/a with x , from the value of 2 expected for the cubic zinc-blende structure, also indicates an increase of the tetragonal distortion as the concentration of magnetic atoms is increased.

As starting models for the distribution of cations, the Mn atoms were allowed to occupy the lattice sites available to cations ($2a$ and $4d$) and the vacant cation sites ($2b$). The refinement of the crystal structure showed that the Mn ions

TABLE I. Mn content (x_{diff}), atomic coordinates for Se ($Y=X$) (Se at special position $8i$; Mn, Zn, and Ga(1) at special position $4d$; Ga(2) at special position $2a$), occupancy factor of Mn (occupancy factor of Mn + occupancy factor of Zn + occupancy factor of Ga(1) = 1.0; Occ(Ga(1)) = 0.5; Occ(Zn) = 0.5 – Occ(Mn); Occ(Ga(2)) = 1.0), lattice parameters, isotropic temperature factors, and conventional goodness-of-fit factors from Rietveld refinement of neutron-diffraction data obtained at 300 K for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$. Space group: tetragonal $I\bar{4}2m$.

x_{diff}	X ITF(4d)	Z ITF(2a)	Occ(Mn) ITF(Se)	a (Å) R_B	c (Å) R_{wp}
0.0	0.264 37(8) 0.34(2)	0.116 45(6) 0.63(3)	0.0 0.230(9)	5.511 77(1) 8.1	10.946 40(2) 2.2
0.104(4)	0.263 91(9) 0.395(24)	0.116 43(6) 0.64(3)	0.052(2) 0.319 5(89)	5.521 58(1) 8.3	10.949 87(2) 2.3
0.240(4)	0.263 80(9) 0.34(3)	0.116 23(6) 0.72(3)	0.120(2) 0.280(8)	5.535 18(1) 9.5	10.949 87(2) 2.3
0.343(4)	0.263 23(8) 0.43(3)	0.116 22(5) 0.89(3)	0.171 5(21) 0.415(7)	5.551 36(1) 7.2	10.954 47(3) 2.0
0.482(4)	0.263 04(10) 0.33(3)	0.115 91(6) 0.84(4)	0.241(2) 0.383 5(79)	5.566 47(1) 8.8	10.943 94(3) 2.1

exclusively occupy the $4d$ lattice sites. Therefore, the magnetic ions occupy the same lattice sites as the Zn atoms in the range $0 < x < 0.5$ (see Table I) and this configuration in which the Mn ions are disordered is more stable than the ones in which the cations are partially or totally ordered (as in the case of MnGa_2Se_4). This fact significantly influences the magnetic properties of the system (see Sec. III B). The Mn content of each sample has been obtained by doubling the occupancy factor of this cation in the corresponding $4d$ lattice site (see Table I).

The main bond distances are shown in Table II. The distance Zn,Mn,Ga($4d$)–Se increases smoothly with x . This is to be expected, since in this type of material the Mn–Se bond distance is larger than the Ga–Se and (Zn,Ga)–Se distances. The bond distances Mn–Se and (Zn,Ga)–Se have been reported to be 2.55(2) and 2.4365(5) Å, respectively, in MnGa_2Se_4 (Ref. 13) and ZnGa_2Se_4 .¹⁴ The partial substitution of Zn by Mn does not change the population of the $2a$ lattice

site and, as expected, the bond distance Ga($2a$)–Se in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 \leq x < 0.5$ is not significantly affected by the substitution process. Its value is in agreement with that reported for ZnGa_2Se_4 [2.4204(10) Å] and MnGa_2Se_4 [2.42(2) Å].

B. Magnetic behavior

The dominant mechanism responsible for the magnetic interaction between Mn ions in DMSs has been found to be superexchange.^{22,23} The evolution of the inverse of the dc magnetic susceptibility data, $1/X$, of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$ as a function of temperature is presented in Fig. 4. These experiments indicate that the systems behave as paramagnets in the temperature range considered. The data have been fitted to a Curie–Weiss law $X = C/(T - \theta)$ over the temperature range 130–250 K to obtain the Curie constant C and the temperature correction θ . The latter takes a positive

FIG. 2. Least-squares fit to the powder neutron diffraction data collected from $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $x=0$ at ambient temperature. The dots are the experimental data points and the solid line is the calculated profile. The lower trace shows the difference (measured minus calculated) divided by the estimated standard deviation on the experimental data points. The tick marks along the top of the figure denote the calculated positions of all the Bragg reflections allowed by $I\bar{4}2m$ symmetry.

FIG. 3. Least-squares fit to the powder neutron diffraction data collected from $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $x=0.482(4)$ at ambient temperature. The dots are the experimental data points and the solid line is the calculated profile. The lower trace shows the difference (measured minus calculated) divided by the estimated standard deviation on the experimental data points. The tick marks along the top of the figure denote the calculated positions of all the Bragg reflections allowed by $I\bar{4}2m$ symmetry.

TABLE II. Main bond distances obtained from Rietveld refinement of neutron-diffraction data taken at 300 K for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$. Space group: tetragonal $I\bar{4}2m$. The Curie–Weiss constant, θ , and the manganese content, x_{mag} , have been calculated from magnetic susceptibility data.

x_{diff}^a	$d[4d\text{-Se}]$ (Å) ^b	$d[2a\text{-Se}]$ (Å) ^b	x_{mag}	θ (K)
0.0	2.438 7(5)	2.423 1(5)	0.0	...
0.104(4)	2.441 7(6)	2.423 3(5)	0.099 ± 0.005	-4 ± 2
0.240(4)	2.446 8(6)	2.425 7(5)	0.24 ± 0.01	-19 ± 2
0.343(4)	2.451 7(5)	2.427 3(5)	0.36 ± 0.02	-36 ± 2
0.482(4)	2.457 1(6)	2.428 4(6)	0.49 ± 0.02	-46 ± 2

^aMn content determined from crystallographic data.

^bMn, Zn, and Ga(1) at special position 4d; Ga(2) at special position 2a; and vacancy at special position 2b.

value in the case of predominantly ferromagnetic interactions and a negative value in the case of predominantly antiferromagnetic ones. Since C depends on the quantity of magnetic ions,²⁴ and therefore on x , it is possible to calculate the content of Mn of each sample from the measured magnetic data. The estimated accuracy of this method is $\pm 5\%$.²⁵ Thus $C = xNg^2\mu_B^2S(S+1)/3k_B$, where x represents, in our case, the fraction of magnetic ions, N is Avogadro's constant, g is the Landé constant, μ_B is the Bohr magneton, S is the spin of the magnetic ion ($5/2$ for Mn^{2+}), and k_B is the Boltzmann constant. Everything is known in the above expression, except the g factor, which has been taken to be that of the Mn ion in MnGa_2Se_4 . This g value can be easily calculated from the experimental Curie constant C for $x=1$.

The expression to calculate the Mn content of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series with $0 < x < 0.5$ is the following: $x = [\alpha C(x)]/[-\beta C(x) + C(x=1)]$, where $C(x)$ is the Curie constant of the dilution x in $\text{emu g}^{-1} \text{K}^{-1}$, $C(x=1)$ is the Curie constant of MnGa_2Se_4 in $\text{emu mol}^{-1} \text{K}^{-1}$, and α and β determine the molecular weight of the series, M_w (g mol^{-1}), through the relationship $M_w = \alpha + \beta x$. The above mathe-

matical expression for x is of general application for a DMS. In the case under study, $\alpha = 520.676 \text{ g mol}^{-1}$ (the molecular weight corresponding to ZnGa_2Se_4) and $\beta = -10.452 \text{ g mol}^{-1}$. The Weiss temperatures θ corresponding to the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series have also been obtained from a Curie–Weiss law fit. Both x and θ values are shown in Table II.

Very different θ and C values can be found for a given series of diluted magnetic semiconductors, depending on the temperature range used for the fitting of the experimental susceptibility data. The knowledge of the x values for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ from neutron powder diffraction data can help in selecting the appropriate temperature range. These Mn contents can be used to calculate a Curie constant, which we have named C_{diff} and the inverse of which gives the slope of the $1/X$ vs T straight line. The slope associated to C_{diff} should be equal, within the experimental error, to that determined by fitting the experimental magnetic data to $1/X = -\theta/C + T/C$. We have used this agreement as a criterion to support the correctness of the temperature range used for the fitting and, therefore, the reliability of the obtained θ values. The agreement between the slopes is equivalent to that between the Mn contents calculated from neutron powder diffraction and magnetic data and is shown in Table II for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$.

The negative values of θ indicate predominantly antiferromagnetic interactions within $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$. MnGa_2Se_4 has been reported to order as an antiferromagnet below $T = 6.4 \pm 0.1 \text{ K}$ with $\theta = -23 \pm 2 \text{ K}$.¹⁵ The mathematical expression for the Weiss temperature is $\theta = [2S(S+1)/3] \sum (z_i J_i / k_B)$, where S is the spin of the magnetic ion ($S = 5/2$ for Mn^{2+}), z represents the number of magnetic neighbors of a given reference ion, and J is the corresponding magnetic superexchange constant.²⁴ The index of the summation refers to the magnetic superexchange pathways with $J \neq 0$. If $z = xz_0$ this expression can be simplified to $\theta(x) = x\theta_0$, where θ_0 and z_0 refer to the undiluted compound. However, in the case of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$, the probability of finding one magnetic ion neighboring another is given by ξ instead of x , where ξ is defined as the occupancy factor of the Mn ion on the 4d lattice site. Therefore, the Weiss temperature can be written as $\theta(\xi) = \xi[2S(S+1)/3] \sum (z_{0,i} J_i / k_B)$ for that series, where $z_{0,i}$ refers to the corresponding magnetically undiluted system and the ξ values are taken from Table I [$\xi = \text{Occ}(\text{Mn})$]. Using this mathematical expression, a global superexchange magnetic constant $\sum (z_{0,i} J_i / k_B) = -36 \pm 5 \text{ K}$ can be estimated by fitting the experimental data for θ vs ξ to a straight line. This global magnetic constant is about one order of magnitude higher than that reported for MnGa_2Se_4 [$\sum (z_{0,i} J_i / k_B) = -3.9 \pm 2 \text{ K}$]¹⁵ for which the magnetic superexchange pathways are of the type $\text{Mn-Se} \cdots \text{Se-Mn}$ with antiferromagnetic constants of around $J/k_B = 0.1\text{--}0.5 \text{ K}$. However Mn-Se-Mn contacts must be also considered in the case of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$. This is a magnetic pathway reported for zinc-blende structured $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$, which exhibits a related crystal structure,²² with a corresponding superexchange constant of -12.2 K .²⁶ Therefore, the existence of higher magnetic interactions associated with shorter

FIG. 4. Evolution of the inverse of the dc magnetic susceptibility with temperature for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$ under an external magnetic field of 1 T.

FIG. 5. Dependence of the Mn–Mn distances with x in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$. The equations used to calculate these distances are depicted on the right-hand side of the figure (a and c are the unit-cell parameters, taken from Table I). The superexchange magnetic constants associated with those distances are also shown on the left-hand side of the figure.

magnetic pathways is shown to play a significant role in the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series when compared to MnGa_2Se_4 .

In the series under study, the magnetic constant between first nearest neighbors can be estimated using the global magnetic constant calculated above. Because only the order of magnitude of the superexchange constants for MnGa_2Se_4 is known,¹⁵ we have used the data published for zinc-blende $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$.²⁶ The exchange pathways are expected to be equivalent due to the similarity of the crystal structures. Those data for $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ provide J_1/k_B , the exchange constant corresponding to Mn–Se–Mn interactions (Mn–Mn distance = $a/\sqrt{2}$ Å, where a is the cubic unit-cell parameter), and three superexchange constants between next-nearest neighbors involving Mn–Se–Se–Mn-type contacts: J_2/k_B (Mn–Mn distance = a Å), J_3/k_B (Mn–Mn distance = $a\sqrt{3}/2$ Å), and J_4/k_B (Mn–Mn distance = $a\sqrt{2}$ Å). In order to simplify the model, we have also assumed that $c/2 \approx a$ and that J_i/k_B ($i=1,2,3,4$) does not change significantly with x . This hypothesis is supported by the evolution of the Mn–Mn distances as a function of x in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$ (see Fig. 5). With these approximations, the Curie–Weiss temperature of this series, $\theta(\xi) = \xi[2S(S+1)/3] \Sigma(z_{0,i}J_i/k_B)$, can be written as $\theta(\xi) = \xi[2S(S+1)/3] [4J_1/k_B + 6J_2/k_B + 8J_3/k_B + 8J_4/k_B]$. Using $\Sigma(z_{0,i}J_i/k_B) = -36$ K (from the previous paragraph) and the exchange constants reported for $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ (Ref 26) ($J_2/k_B = -0.2$ K, $J_3/k_B = -0.1$ K, and $J_4/k_B = -0.4$ K), a value of $J_1/k_B = -7.7$ K can be deduced from the expression $\Sigma(z_{0,i}J_i/k_B) = [4J_1/k_B + 6J_2/k_B + 8J_3/k_B + 8J_4/k_B]$. In the case of the zinc-blende structure, $J_1/k_B = -12.2$ K.²⁶ Due to the approximations introduced, $J_1/k_B = -7.7$ K should, of course, be regarded as an estimate of the order of magnitude of J_1/k_B in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$.

One interesting aspect of the series under study is that the lattice sites available to the magnetic cations are not the same in MnGa_2Se_4 (2d) as in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$ (4d). As a consequence, the magnetically undiluted system corresponding to $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$ is not MnGa_2Se_4 but, rather, a hypothetical compound for which the magnetic atoms are distributed at random over the 4d lattice sites of space group $\bar{I}42m$ with 50% occupancy. The Curie–Weiss temperature of such a magnetically undiluted archetype system can be estimated using the expression $\theta = \xi [2S(S+1)/3] \Sigma(z_{0,i}J_i/k_B)$ with $\xi = 0.5$ (that is, $x = 1$) and the previously derived value $\Sigma(z_{0,i}J_i/k_B) = -36$ K. Thus, a value of $\theta(x=1, \bar{I}42m) = -105$ K can be calculated. As expected, the Curie–Weiss temperature of that hypothetical system, $\theta(x=1; \bar{I}42m)$, is higher than that of the real undiluted compound MnGa_2Se_4 , $\theta(\text{MnGa}_2\text{Se}_4) = -23$ K,¹⁵ which exhibits a completely ordered distribution of magnetic ions. The reason is, once again, the creation of the superexchange pathway Mn–Se–Mn with a stronger associated magnetic constant in the case of $\bar{I}42m$ symmetry. A search of the literature to find a real magnetically undiluted compound in which the Mn ions are distributed at random over the 4d lattice sites of $\bar{I}42m$ symmetry (50% occupancy) shows that MnIn_2Te_4 fulfils these requirements. Interestingly, the Curie–Weiss constant of this material has been found to be $\theta(\text{MnIn}_2\text{Te}_4) = -88 \pm 10$ K,²⁷ which compares well with that of our hypothetical system $\theta(x=1; \bar{I}42m) = -105$ K.

IV. CONCLUSIONS

$\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$ retains the crystal symmetry of the parent ZnGa_2Se_4 , with a defective stannite structure described by the tetragonal space group $\bar{I}42m$. Although the magnetic cations are completely ordered onto a particular lattice site in MnGa_2Se_4 , the controlled substitution of Zn by Mn in ZnGa_2Se_4 ($0 < x < 0.5$) results in complete disorder of the magnetic ions over the corresponding crystallographic position. A tendency to cation ordering as the content of Mn increases is suggested by the decrease of the unit-cell parameter c/a with x .

The disordered distribution of the Mn ions has a profound effect on the magnetic behavior of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 0.5$. The magnetically undiluted system corresponding to that series is not MnGa_2Se_4 but, instead, a hypothetical compound for which the magnetic atoms are distributed at random over the 4d lattice sites of space group $\bar{I}42m$ with 50% occupancy. Moreover, the global magnetic interaction between manganese ions is found to be significantly higher than that expected for the classical magnetic dilution of the end member of the series MnGa_2Se_4 .

The distance between the Mn ions along the various magnetic superexchange pathways is not significantly affected by the degree of magnetic dilution. This finding suggests that the magnetic superexchange constants do not vary significantly with x along the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series with $0 < x < 0.5$. In addition, a method of general application is provided for the selection of the appropriate range of temperature to calculate a correct Weiss constant θ in DMSs.

The method is based on the precise knowledge of the concentration of magnetic ions within the sample and their influence on the Curie constant C .

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