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 $\text{MnGa}_2\text{Se}_4$ (the magnetic end member of the series with $I4$ 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 $\text{MnGa}_2\text{Se}_4$. A generally applicable method for the calculation of the correct Weiss temperature $\theta$ 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.\textsuperscript{1,2} Specific properties and requirements are matched by tailoring the composition through the use of solid solutions,\textsuperscript{3,4} though significant differences between the crystal structure of magnetic materials and a nonmagnetic host can make the two systems incompatible with each other.\textsuperscript{5}

The degree of atomic ordering critically influences the physical properties (optical, electronic, magnetic,…) of the material.\textsuperscript{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.\textsuperscript{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.\textsuperscript{9} One of the problems encountered in DMSs is that most of these systems, particularly pseudobinary DMSs, exhibit comparatively higher $\theta$ values.\textsuperscript{10} This makes the calculation of reliable Weiss temperatures more difficult due to experimental limitations on the available temperature range.

$\text{Mn}^{2+}$ is a magnetic ion with spin $S=5/2$. $\text{ZnGa}_2\text{Se}_4$ and $\text{MnGa}_2\text{Se}_4$ are semiconductors showing direct gaps of around 2.3 and 2.5 eV, respectively.\textsuperscript{11,12} The controlled substitution of Zn ions by Mn in $\text{ZnGa}_2\text{Se}_4$ 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 $\text{ZnGa}_2\text{Se}_4$ and defective chalcopyrite for $\text{MnGa}_2\text{Se}_4$), a high degree of miscibility is expected. Moreover, $\text{MnGa}_2\text{Se}_4$ exhibits a totally ordered scheme of the magnetic cations while $\text{ZnGa}_2\text{Se}_4$ shows a completely disordered arrangement of the Zn atoms.\textsuperscript{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 $\text{MnGa}_2\text{Se}_4$ orders magnetically below $6.4\pm0.1$ K.\textsuperscript{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 $\theta$ 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.\textsuperscript{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
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 diffractometer 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 $0.5 < d(\text{Å}) < 12.0$. Normalization of the data and correction for sample absorption were carried out using the GE-NIE software. The program TF14LS, based on the CAMBRIDGE CRYSTALLOGRAPHIC SUBROUTINE LIBRARY, was used for Rietveld analysis of the diffraction patterns. Refinements of the crystal structure were carried out using the data in the range $0.8 < d(\text{Å}) < 3.2$ obtained using the highest-resolution backscattering detectors, which possess an essentially constant resolution of $\Delta d/d = 5 \times 10^{-3}$.

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$_2$Se$_4$ and MnGa$_2$Se$_4$ were used as the starting models for the determination of the structural arrangement of atoms within Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ with $0 < x < 0.5$. ZnGa$_2$Se$_4$ crystallizes in the tetragonal space group $I42m$ possessing a defective stannite structure\textsuperscript{14} 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 Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ series is MnGa$_2$Se$_4$. The crystal structure of this magnetic material is 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 $I4$, with $a=5.677(1)$ Å and $c=10.761(2)$ Å.\textsuperscript{13} The key difference between the crystal structure of the two end members of the series is the absence of cation disorder in MnGa$_2$Se$_4$. 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 Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ with $0 < x < 0.5$ 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$_2$Se$_4$) or ordered (as in MnGa$_2$Se$_4$). 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 $I42m$. While the reflection conditions for space groups $I4$ and $I42m$ 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 $I4$, but equal for $I42m$. The refinements performed on the Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ with $0 < x < 0.5$ series using $I4$ 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 Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ with $0 < x < 0.5$. 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.\textsuperscript{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...
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 MnGa2Se4). 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 MnGa2Se4 (Ref. 13) and ZnGa2Se4.14 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 Zn1−xMnGa2Se4 with \(0 < x < 0.5\) is not significantly affected by the substitution process. Its value is in agreement with that reported for ZnGa2Se4 [2.4204(10) Å] and MnGa2Se4 [2.42(2) Å].

### TABLE I. Mn content (\(x_{\text{eff}}\)), atomic coordinates for Se (\(Y=\infty\)) (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 Zn1−xMn,xGa2Se4. Space group: tetragonal \(I\bar{4}2m\).

| \(x_{\text{eff}}\) | \(X\) ITF(4d) | \(Z\) ITF(2a) | Occ(Mn) ITF(Se) | \(a\) (Å) | \(c\) (Å) | \(R_I\) | \(R_{wp}\) |
|------------------|----------------|----------------|----------------|---------|---------|-------|-------|
| 0.0              | 0.264 37(8)    | 0.116 45(6)    | 0.0            | 5.511 77(1) | 10.946 40(2) | 8.1     | 2.2   |
| 0.04(4)          | 0.263 91(9)    | 0.116 43(6)    | 0.052(2)       | 5.521 58(1) | 10.949 87(2) | 8.3     | 2.3   |
| 0.104(4)         | 0.263 80(9)    | 0.116 23(6)    | 0.120(2)       | 5.535 18(1) | 10.949 87(2) | 9.5     | 2.0   |
| 0.240(4)         | 0.263 28(3)    | 0.116 22(5)    | 0.171 5(21)    | 5.551 36(1) | 10.954 47(3) | 7.2     | 2.0   |
| 0.343(4)         | 0.263 04(10)   | 0.115 91(6)    | 0.241(2)       | 5.566 47(1) | 10.943 94(3) | 8.8     | 2.1   |

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 Zn1−xMnGa2Se4 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 \(\theta\). The latter takes a positive

![FIG. 2. Least-squares fit to the powder neutron diffraction data collected from Zn1−xMn,xGa2Se4 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 Zn1−xMn,xGa2Se4 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.]
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, 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 ±5%. Thus $C = xN \mu_B^2 S(S+1)/3k_B$, where $x$ represents, in our case, the fraction of magnetic ions, $N$ is Avogadro’s constant, $\mu_B$ is the Landé constant, $\mu_B$ 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$_2$Se$_4$. 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 Zn$_{1-x}$Mn$_x$Ga$_2$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 emu g$^{-1}$ K$^{-1}$. $C(x=1)$ is the Curie constant of MnGa$_2$Se$_4$ in emu mol$^{-1}$ K$^{-1}$, and $\alpha$ and $\beta$ determine the molecular weight of the series, $M_w$ (g mol$^{-1}$), through the relationship $M_w = \alpha + \beta x$. The above mathematical expression for $x$ is of general application for a DMS. In the case under study, $\alpha = 520.676$ g mol$^{-1}$ (the molecular weight corresponding to ZnGa$_2$Se$_4$) and $\beta = -10.452$ g mol$^{-1}$. The Weiss temperatures $\theta$ corresponding to the Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ series have also been obtained from a Curie–Weiss law fit. Both $x$ and $\theta$ values are shown in Table II.

Very different $\theta$ 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 Zn$_{1-x}$Mn$_x$Ga$_2$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 $C_{\text{diff}}$ and the inverse of which gives the slope of the $1/X$ vs $T$ straight line. The slope associated to $C_{\text{diff}}$ should be equal, within the experimental error, to that determined by fitting the experimental magnetic data to $1/X = -\theta/(C+T)$. 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 $\theta$ 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 Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ with $0<x<0.5$.

The negative values of $\theta$ indicate predominantly antiferromagnetic interactions within Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$. MnGa$_2$Se$_4$ has been reported to order as an antiferromagnet below $T = 6.4 \pm 0.1$ K with $\theta = -23 \pm 2$ K. The mathematical expression for the Weiss temperature is $\theta = [2S(S+1)/3] \Sigma z_i J_i/k_B$, where $S$ is the spin of the magnetic ion (5/2 for Mn$^{2+}$), $z$ represents the number of magnetic neighbors of a given reference ion, and $J_i$ is the corresponding magnetic superexchange constant. The index of the summation refers to the magnetic superexchange pathways with $J_i 
eq 0$. If $z = \bar{z}$, this expression can be simplified to $\theta(x) = x \theta_0$, where $\theta_0$ refer to the undiluted compound. However, in the case of Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ with $0<x<0.5$, the probability of finding one magnetic ion neighboring another is given by $\xi$ instead of $x$, where $\xi$ is defined as the occupancy factor of the Mn ion on the 4$d$ lattice site. Therefore, the Weiss temperature can be written as $\theta(x) = \xi [2S(S+1)/3] \Sigma z_i J_i/k_B$ for that series, where $\xi_0$ refers to the corresponding magnetically undiluted system and the $x$ values are taken from Table I. Using this mathematical expression, a global superexchange magnetic constant $\Sigma (z_i J_i/k_B) = -36.5 \pm 5$ K can be estimated by fitting the experimental data for $\theta$ vs $\xi$ to a straight line. This global constant is about one order of magnitude higher than that reported for MnGa$_2$Se$_4$ [\Sigma (z_0 J_i/k_B) = -3.9 \pm 2$ K] for which the magnetic superexchange pathways are of the type Mn–Se–Mn with anti-ferromagnetic constants of around $J/k_B = 0.1–0.5$ K. However Mn–Se–Mn contacts must be also considered in the case of Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ with $0<x<0.5$. This is a magnetic pathway reported for zinc-blende structured Zn$_{1-x}$Mn$_x$Se, which exhibits a related crystal structure, with a corresponding superexchange constant of $-12.2$ K. Therefore, the existence of higher magnetic interactions associated with shorter

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

| $x_{\text{mag}}$ | $d[4d-Se]$ (Å) | $d[2a-Se]$ (Å) | $\theta$ (K) |
|------------------|----------------|----------------|-------------|
| 0                | 2.438 (7)      | 2.423 (5)      | 0.0         |
| 0.104 (4)        | 2.441 (7)      | 2.423 (5)      | 0.099±0.005 | $-4\pm2$ |
| 0.204 (5)        | 2.446 (8)      | 2.425 (7)      | 0.24±0.01   | $-19\pm2$ |
| 0.304 (4)        | 2.451 (7)      | 2.427 (5)      | 0.36±0.02   | $-36\pm2$ |
| 0.482 (4)        | 2.457 (11)     | 2.428 (6)      | 0.49±0.02   | $-46\pm2$ |

$^a$Mn content determined from crystallographic data.

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

![Figure 4](image-url) Evolution of the inverse of the dc magnetic susceptibility with temperature for Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ with $0<x<0.5$ under an external magnetic field of 1 T.
magnetic pathways is shown to play a significant role in the 
Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ series when compared to MnGa$_2$Se$_4$.

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$_2$Se$_4$

is known, we have used the data published for zinc-blende 
Zn$_{1-x}$Mn$_x$Se. The exchange pathways are expected to be 
equivalent due to the similarity of the crystal structures. 
Those data for Zn$_{1-x}$Mn$_x$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–Mn–type contacts: $J_2/k_B$ (Mn–Mn 
distance $=a$ Å), $J_3/k_B$ (Mn–Mn distance $=a/3/2$ 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 = 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 Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ with 
$0 < x < 0.5$ (see Fig. 5). With these approximations, the 
Curie–Weiss temperature of this series, $\theta(\xi) = \xi [2S(S+1)/3] \Sigma(x_0,J_i/k_B)$, can be written as 
$\theta(\xi) = \xi [2S(S+1)/3] [4J_1/k_B + 6J_2/k_B + 8J_3/k_B + 8J_4/k_B] \Sigma(x_0,J_i/k_B)$. Using $\Sigma(x_0,J_i/k_B) = -36$ K
(from the previous paragraph) and the exchange constants 
reported for Zn$_{1-x}$Mn$_x$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 $\Sigma(x_0,J_i/k_B) = [4J_1/k_B + 6J_2/k_B + 8J_3/k_B + 8J_4/k_B]$. In the case of the zinc-blende structure, $J_1/k_B = -12.2$ K.

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 
Zn$_{1-x}$Mn$_x$Ga$_2$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$_2$Se$_4$ (2$d$) as in Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ with $0 < x < 0.5$ (4$d$). As a consequence, the magnetically undiluted 
system corresponding to Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ with $0 < x < 0.5$ is 
not MnGa$_2$Se$_4$ but, rather, a hypothetical compound for 
which the magnetic atoms are distributed at random over the 
4$d$ lattice sites of space group $I42m$ with 50% occupancy. The Curie–Weiss temperature of such a magnetically undiluted archetype system can be estimated using the expression 
$\theta = \xi [2S(S+1)/3] \Sigma(x_0,J_i/k_B)$ with $x = 0.5$ (that is, $x = 1$) and the previously derived value $\Sigma(x_0,J_i/k_B) = -36$ K. Thus, a value of $\theta(x=1;I42m) = -105$ K can be calculated. As expected, the Curie–Weiss temperature of this hypothetical system, $\theta(x=1;I42m)$, is higher than that of the real undiluted compound MnGa$_2$Se$_4$, $\theta$(MnGa$_2$Se$_4$) = -23 K, 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 $I42m$ symmetry. A search of the literature to find a real magnetically undiluted compound in which the Mn ions are distributed at random over the 4$d$ lattice sites of $I42m$ symmetry (50% occupancy) shows that MnIn$_2$Te$_4$ fulfills these requirements. Interestingly, the Curie–Weiss constant of this material has been found to be $\theta$(MnIn$_2$Te$_4$) = -88±10 K, which compares well with that of our hypothetical system $\theta(x=1;I42m) = -105$ K.

**IV. CONCLUSIONS**

Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ with $0 < x < 0.5$ retains the crystal 
symmetry of the parent ZnGa$_2$Se$_4$, with a defective stannite 
structure described by the tetragonal space group $I42m$. 
Although the magnetic cations are completely ordered onto a 
partial lattice site in MnGa$_2$Se$_4$, the controlled substitution 
of Zn by Mn in ZnGa$_2$Se$_4$ ($0 < x < 0.5$) 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 Zn$_{1-x}$Mn$_x$Ga$_2$Se$_4$ 
with $0 < x < 0.5$. The magnetically undiluted system 
corresponding to this series is not MnGa$_2$Se$_4$ but, instead, a 
hypothetical compound for which the magnetic atoms are 
distributed at random over the 4$d$ lattice sites of space group 
$I42m$ 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$_2$Se$_4$.

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 Zn$_{1-x}$Mn$_x$Ga$_2$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 $\theta$ 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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