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Nuclear-magnetic-resonance study and simulation of the spin configuration in In- and Ga-substituted $CdCr_2S_4$

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The hyperfine fields at the nuclei of Cd^{2+}, Ga^{3+}, and In^{3+} ions in the substituted ferromagnetic spinel $CdCr_2S_4$ have been measured by the spin-echo method at liquid-helium temperature. The impurity, when located at the B site, produces a large shift in the resonance frequency of the Cd^{2+} ions nearest to it, and shows an anomalous field dependence of its own resonance frequency. A well-defined canted spin structure was then deduced from these NMR data. Such a structure was reproduced by simulation on a system of $N=1185$ spins, taking into account all positive nearest-neighbor and negative third-neighbor pair interactions plus local interactions around the impurity. The simulation results showed that these local interactions must be introduced in order to create the canted spin structure, and are much greater than the original ones. This strong effect was ascribed to the superexchange interaction via the impurity s valence electron whose spin density, as deduced from the hyperfine interaction, is unusually high.

I. INTRODUCTION

Recently, a spin-glass state was reported in the dilute spinel compound $CdCr_{2x}In_{2-2x}S_4$ (Ref. 1) at concentrations of magnetic ions as high as $x=0.85$. In the dilute compound $Eu_xSr_{1-x}S$,[2] the spin-glass state appears in the concentration range $0.1<x<0.5$. In these insulating systems the nearest-neighbor superexchange interaction is positive and the frustration arises from the further nearest-neighbor negative interactions. The question was whether the substituted diamagnetic cations modify significantly the superexchange interactions in their neighborhood.

In this paper we report NMR measurements performed on In- and Ga-substituted $CdCr_2S_4$ ferromagnetic spinels. The NMR results showed a canted spin structure around the impurity. In the next section we present a simulation of the magnetic structure using a local exchange parameter. We then discuss the origin of this local interaction.

II. EXPERIMENTAL DETAILS

The compounds $CdCr_{2x}In_{2-2x}S_4$ and $CdCr_{2x}Ga_{2-2x}S_4$ were prepared from CdS, Cr_2S_3, Ga_2S_3, and In_2S_3. The starting materials were carefully mixed in an agate mortar and then pressed into pellets which were dried in quartz tubes while pumping for 2 h. After sealing these evacuated quartz tubes, the samples were heated to 850 °C at 17 °C/h. They were held at this temperature for 1 d and then furnace-cooled.

The NMR measurements were done at liquid-helium temperature by using a variable-frequency spin-echo apparatus with pulse amplitude up to 3 kV. The sample was put in a Dewar tail around which is fitted the exciting coil of the spectrograph. A dc magnetic field up to 12 kOe can be applied perpendicularly to the coil axis.

III. NMR RESULTS AND INTERPRETATION

In insulating ferromagnets the internal field at the nucleus of a diamagnetic cation is due mainly to the polarization of the s valence electrons produced by the nearest-neighbor magnetic ions. The value of the hyperfine field on Cd nuclei in $CdCr_2S_4$ was already reported[3] to be $+168$ kOe, that is, $h=\frac{168}{12}=14$ kOe per Cr^{3+} spin. For the Cd sites which are surrounded by eleven Cr^{3+} ions and one substituted diamagnetic cation, the expected value of the hyperfine field is $11h=154$ kOe for a ferromagnetic arrangement. The actual situation is illustrated in Fig. 1 by the relative shift of the satellite Cd lines, which is much greater than the above value of $\frac{1}{12}$. The large de-

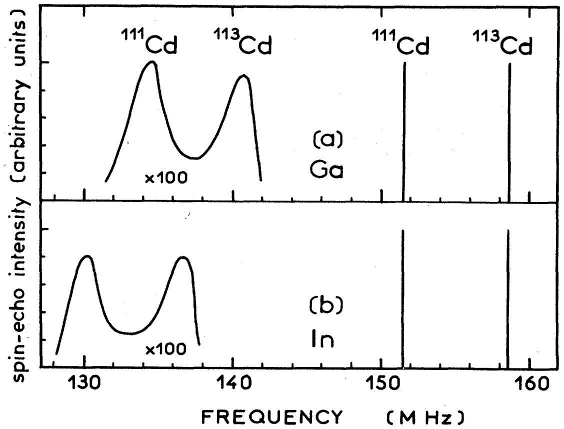

FIG. 1. Resonance spectra of ^{111}Cd and ^{113}Cd in $CdCr_{1.997}X_{0.003}S_4$. (a) $X=Ga$; (b) $X=In$. The low-frequency spectra are due to the Cd nearest neighbor to an impurity at the B site.

crease in the corresponding hyperfine field, 23.2 and 18.6 kOe for the In- and Ga-substituted samples, respectively, is the sign of a canted spin structure around the impurity.

We also observed the resonance signals of ^{115}In, ^{69}Ga, and ^{71}Ga in the substituted compounds with $1-x=0.15$ at. %. The NMR data are given in Table I. The In and Ga hyperfine fields are unusually high, about 3 times greater than those in substituted garnets.[4] As shown in Fig. 2, the resonance frequencies increase linearly with the applied magnetic field, but with a slope several times greater than that expected for a ferromagnetic structure. A similar effect was observed by Berger, Budnick, and Burch[5,6] in the metamagnetic spinel $HgCr_2S_4$, which has a flat spiral structure.[7] These authors found the strong field dependence of the frequency to be a result of the changing spin structure. This clearly confirms that the six spins surrounding the impurity are canted with respect to the ferromagnetic direction. Moreover, the canting angle α depends on the external field. The resonance field can be written as

$$H_{\text{imp}}=H_n \cos\alpha+H_0 \ , \tag{1}$$

where H_0 is the external field minus the demagnetizing field of about 1.5 kOe, and H_n is the hyperfine field extrapolated at zero canting angle.

TABLE I. NMR data of In and Ga impurities at *A* and *B* sites in $CdCr_2S_4$ at 2 °K.

Isotopes	Resonance frequency (MHz)	Linewidth (MHz)
	B sites	
^{115}In	397	10
^{69}Ga	237	7
^{71}Ga	300	7
	A sites	
^{115}In	178.1	0.2
^{69}Ga	87.3	~0.3
^{71}Ga	110.9	~0.3

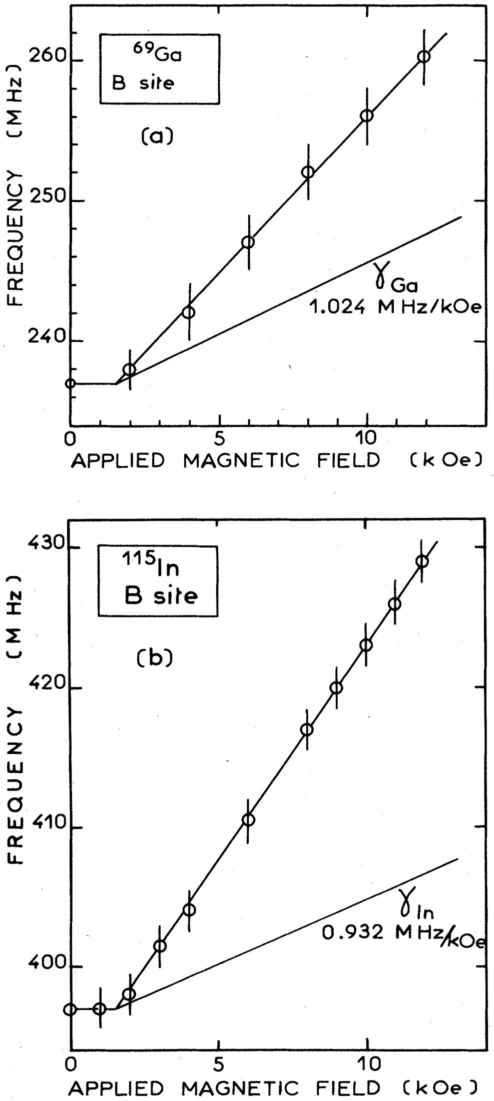

FIG. 2. Field dependence of the nuclear resonance frequency of the impurity at the *B* site. (a) Gallium impurity; (b) indium impurity.

In addition to the NMR signals from In and Ga at the octahedral *B* sites, we observed resonance lines from impurities at the tetrahedral *A* sites. As seen in Table I, these lines are very sharp, reflecting the cubic symmetry of the *A* site. The field dependence of the In resonance frequency is that expected for a standard ferromagnet (Fig. 3) showing the absence of local spin canting. The Ga signal was too small to be observed in an external field. From spin-echo intensities we deduced that the majority of impurity atoms enters the *B* sites, whereas only about one-tenth is substituted on the *A* sites.

IV. SIMULATION OF SPIN STRUCTURE AND COMPARISON WITH NMR RESULTS

Following Dwight and Menyuk,[8] who analyzed the exchange interactions in ferromagnetic chromium spinels, we assume, in a first approximation, that the Heisenberg spin Hamiltonian contains only positive nearest-neighbor

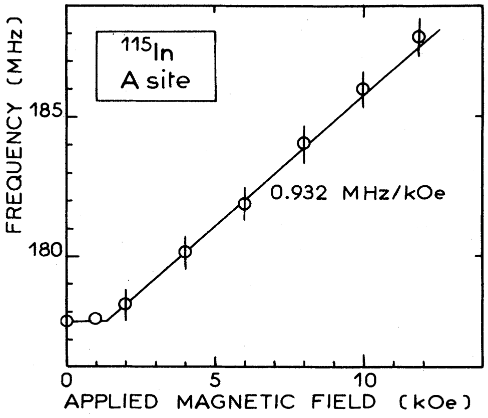

FIG. 3. Field dependence of the ^{115}In resonance frequency at the *A* sites.

and negative third-nearest-neighbor exchange parameters, J_1 and J_3, plus a Zeeman term:

$$\mathscr{H} = -2J_1 \sum_{i>j} \vec{S}_i \cdot \vec{S}_j - 2J_3 \sum_{i>k} \vec{S}_i \cdot \vec{S}_k - g\beta \vec{H}_0 \sum_{i} \vec{S}_i \ . \quad (2)$$

There are six nearest neighbors and twelve third-nearest neighbors. We neglected here the magnetic anisotropy which is very low in these systems.

At low temperature the reduced magnetization varies as $1-AT^{3/2}$. Following the procedure given by Kaplan[9] for spin waves in the spinel lattice, we obtain

$$A = (1.06\times 10^{-2})(J_1+8J_3)^{-3/2}k^{3/2} \ . \quad (3)$$

On the other hand, the paramagnetic Curie temperature is given by the expression

$$\Theta = (2/3k)S(S+1)(6J_1+12J_3) \ . \quad (4)$$

Using the experimental values[10] $A = 10^{-3}k^{3/2}(\mathrm{K})^{-3/2}$ and $\Theta = 152$ K, J_1/k and J_3/k were deduced to be $+11.9$ and -0.88 K, respectively.

In addition, we had to introduce a local exchange parameter J_L which replaces J_3 in the case of a 180° superexchange interaction via the impurity (see Fig. 9).

There is no simple analytical method to obtain the ground state of the Hamiltonian (2) in the presence of diamagnetic impurities. We then developed a computer program which simulates the relaxation of N classical spins from an initial configuration, generally a randomly disordered one, to an equilibrium state. The program uses the following algorithm:

Energy is first minimized with respect to the orientation of a given spin $\vec{S}_i$ by aligning it along the local magnetic field $\vec{H}_i$,

$$\vec{H}_i = \vec{H}_0 + (1/\beta)\sum_{j} J_{ij}\vec{S}_j \ . \quad (5)$$

The same procedure is then repeated spin after spin. This sweep over the N spins is done 20 times, after which the energy of the new spin configuration is calculated and compared to the former value. The entire process starts again until the energy does not vary any more within the computer accuracy of about 10^{-10}.

The present calculations were performed on an Apple II microcomputer using a small spherical subcrystal containing up to 1185 B sites of the spinel structure, each occupied by a spin, except for the center, which represents the diagmagnetic impurity. Different boundary conditions could be applied. The small crystal was either isolated or enclosed in a larger ferromagnetic crystal. Since the spins at equilibrium are expected to lie in the same plane, we

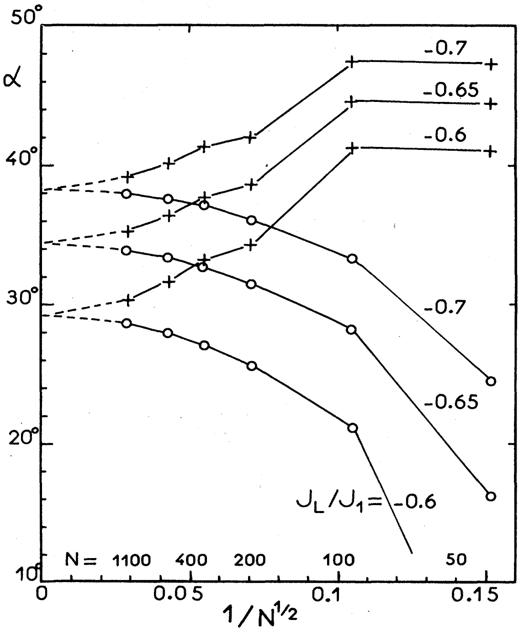

FIG. 4. Canting angle α vs $N^{-1/2}$ for various values of the local exchange parameter, as deduced from the simulation of N spins in a subcrystal with two different boundary conditions: crystal either isolated (×) or enclosed in a ferromagnetic medium (○).

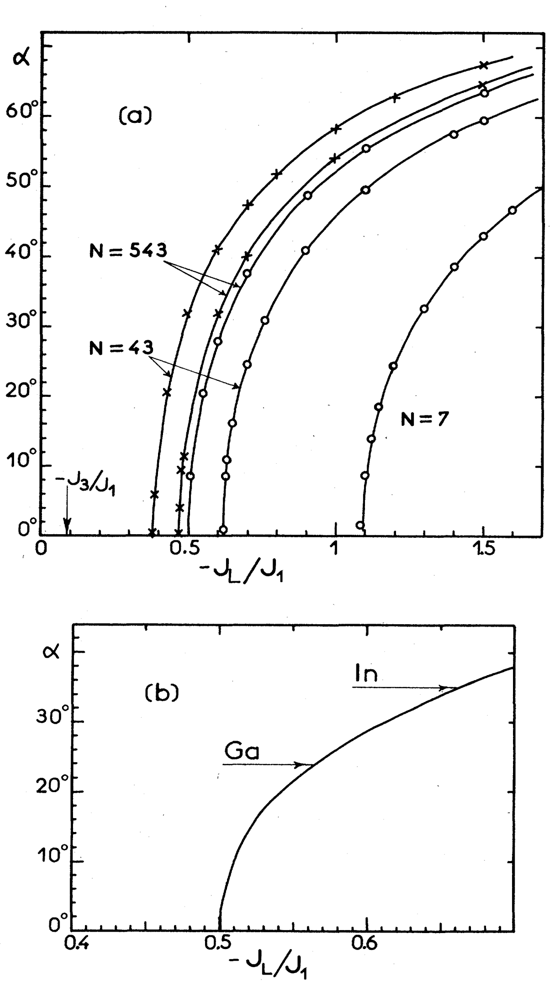

FIG. 5. Canting angle α vs reduced local exchange parameter J_L/J_1 for different N values, as deduced from the simulation of N spins in a subcrystal with two different boundary conditions: crystal either isolated (×) or enclosed in a ferromagnetic medium (○). (a) For $n=7$ the simulated results (○) practically coincide with the solid line representing the analytical expression (6). (b) Detailed variation of α in the experimental range for $N=1185$ spins.

used classical spins with only two components, thus reducing computation time and memory size.

For a given value of J_L, one obtains one spin configuration, and particularly the canting angle α of the six spins surrounding the impurity. As shown in Fig. 4 this canting angle depends on N and on the boundary conditions. At small N values the change in actual shape of the crystals induces some irregularities in the variation of α. Nevertheless, the canting angle reaches practically a limit for $N > 700$. This value corresponds to an impurity concentration of $\frac{1}{700}$, which is close to the experimental one. In other words, the impurity-pair effects are negligible for this concentration range. Afterward, a sphere of $N = 1185$ sites enclosed in a ferromagnetic crystal was used for comparison with experiments. An important result is that the system remains ferromagnetic for small values of J_L (Fig. 5), and the canted structure appears suddenly when $|J_L|$ exceeds a threshold value of $0.5J_1$, which is much greater than $|J_3|$. An analytical solution can be obtained in the simple case of $N = 7$ with similar J_L dependence of the canting angle, but with a higher threshold value (Fig. 5). It is given by the expression

$$\cos\alpha = -(3J_1 + 11J_3)/2J_L \ . \tag{6}$$

A typical arrangement of the spins around the impurity is shown in Fig. 6.

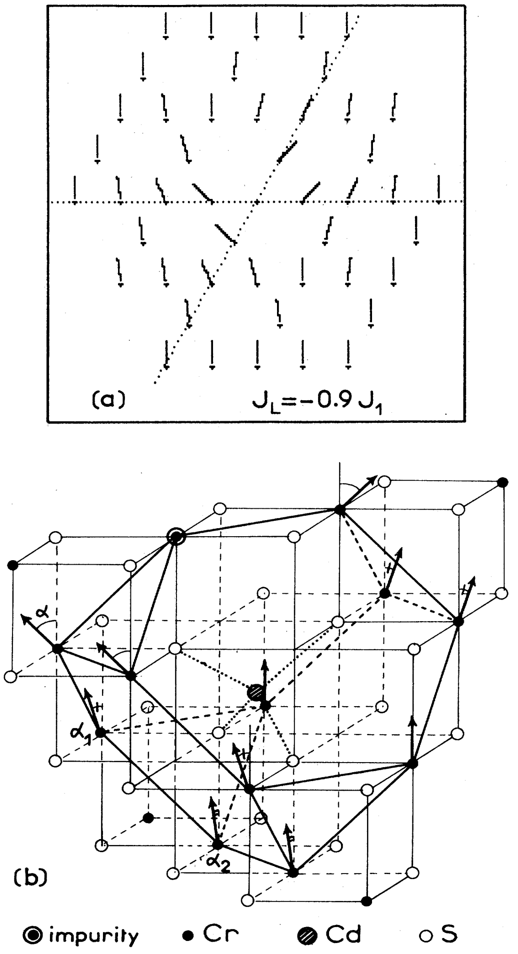

FIG. 6. (a) Typical spin structure with components lying in a (111) plane for $N = 199$ as displayed on a microcomputer screen. The dotted lines are (110)-like directions. (b) Spin structure around a Cd^{2+}-ion nearest neighbor to an impurity as deduced from the simulation of 1185 spins.

The effect of the impurity on the Cd hyperfine interaction is slightly intricate. A Cd^{2+} ion nearest the impurity "sees" 11 nearest-neighbor spins: three with canting angle α, four with angle α_1, two with angle α_2, and two uncanted spins (Fig. 6). Hence the two components of its hyperfine field, parallel and perpendicular to the ferromagnetic direction, can be written as

$$H_{\parallel} = h(3\cos\alpha + 4\cos\alpha_1 + 2\cos\alpha_2 + 2) \ , \quad H_{\perp} = h\sin\alpha \ , \tag{7}$$

where $h = 14$ kOe is the transferred hyperfine field per Cr^{3+} spin as introduced in Sec. III.

The ratios α_1/α and α_2/α_1 are shown by simulation to have the same value of about 0.4, and this is practically independent of $|J_L|$ up to at least $0.7J_1$. From the frequencies of the Cd satellites lines, and using expression (7), the canting angles α are evaluated to be 24° and 35° for Ga and In impurities, respectively. By comparison with the simulation results (Fig. 5), we deduced the corresponding J_L/k values to be -6.7 and -7.9 K, respectively, as compared to $J_3/k = -0.88$ K. It should be pointed out that the experimental uncertainty in α values has only little effect on J_L, as shown in Fig. 5.

The values of the extrapolated hyperfine field H_n appearing in expression (1) are then $+253$ and $+520$ kOe for Ga^{3+} and In^{3+}, respectively. In order to compare the field dependence of In and Ga hyperfine fields, $H_n\cos\alpha$, with simulation results, $\cos\alpha$ values were plotted against the effective magnetic field H_0 (Fig. 7). In the same manner, the field dependence of the perturbed Cd^{2+} hy-

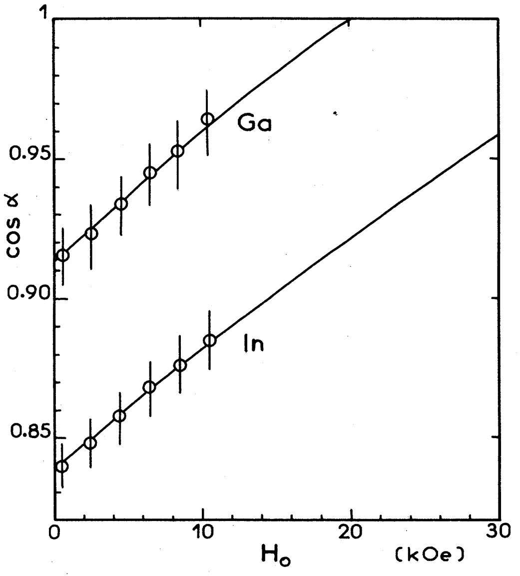

FIG. 7. Experimental $\cos\alpha$ values vs effective applied magnetic field H_0 as compared to simulated results (solid line) for 1185 spins.

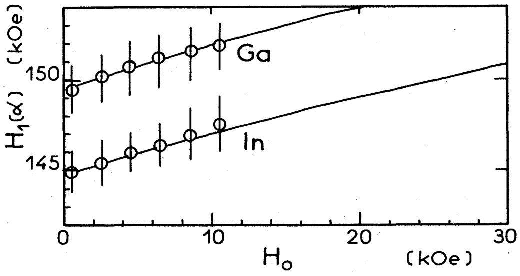

FIG. 8. Field dependence of the hyperfine field $H_1(\alpha)$ of a Cd^{2+}-ion nearest neighbor to an impurity as compared to simulated results using expression (7) (solid line).

perfine field $H_1(\alpha)$ represented by the expression (7) was compared to experimental results (Fig. 8). The agreement is quite satisfactory, showing that the canted structure indeed arises from a strong local exchange interaction around the impurity.

V. DISCUSSION

To see how the impurity can contribute to the exchange interaction, we first deduced, from the H_n values, the fractions f_s of unpaired spin to be 3.7% and 4.6% for the Ga 4s and In 5s electrons, respectively. These values are 2.7 times higher than those at the A sites. The important point is that the s valence-electron densities are usually 1 order of magnitude greater than the f_s values.[4] This shows that the diagmagnetic cation at the B site can play an effective role in the exchange mechanism, depending on the ion-ion overlap in the exchange path (Fig. 9). To see whether this contribution is significant or not, the overlap integrals $S(3p_\sigma,5s)$ and $S(3p_\sigma,3p_\sigma)$ were evaluated at the respective internuclear sulfur-indium and sulfur-sulfur distances. The orbital exponent of the Slater-type functions is nearly the same for the sulfur 3p and indium 5s orbitals.[11] Assuming an orbital exponent of 1.827 (Ref. 11) and using Mulliken's formulas,[12] we calculated the equicenter overlap integrals: $S(3p_\sigma,5s)=0.211$ and $S(3p_\sigma,3p_\sigma)=0.038$. Following the arguments given in Ref. 8, the ratio of the exchange parameter via the impurity over the original one (Fig. 9) should be given by

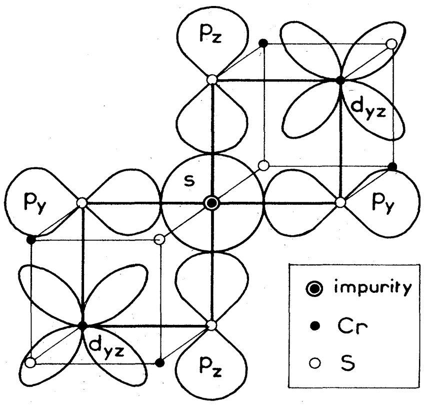

FIG. 9. Superexchange path via the impurity s valence electron.

$$|S(3p_\sigma,5s)|^4/|\tfrac{1}{2}S(3p_\sigma,3p_\sigma)|^2=5.5\,,$$

taking into account the relative orientation of the 3p orbitals and neglecting the $3p_\pi$-$3p_\pi$ overlap. The J_L value represents, in fact, $J_{\text{imp}}+J_3$, where J_{imp} is the contribution of the impurity to the exchange interaction. The above ratio $J_{\text{imp}}/J_3=5.5$ explains qualitatively our experimental values of 6.6 and 8 for Ga and In impurities, respectively. Some contribution from the p valence electron of the impurities to the local interaction can not be excluded. This strong negative local exchange interaction should be the origin of the spin-glass state observed at high magnetic concentration.

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