Three-Spin Interaction in $CsMn_{0.28}Mg_{0.72}Br_3$

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The inelastic-neutron-scattering technique was used to measure the magnetic excitation spectrum of Mn^{2+} triads in $CsMn_{0.28}Mg_{0.72}Br_3$. It is shown that biquadratic two-spin and particularly three-spin interaction terms distinctly contribute to the spin coupling of the Mn^{2+} ions. The present work thus provides direct experimental evidence of the existence of three-body forces in an interacting system.

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The interpretation of physical properties of cooperative systems is generally based on models which are built up in terms of pair interactions. Although the concept of two-body interactions is only an approximation, its wide application is justified by the lack of experimental evidence for the existence of n-body interactions ($n > 2$). Nevertheless, there are indications for important effects of many-body forces in various fields, e.g., effects on the correlations in disordered binary alloys,[1] on the spin coupling of polynuclear transition-metal complexes,[2] on the spin structure of solid ^3He,[3] on the stability of nuclear matter,[4] etc. In all these cases, however, the importance of many-body forces was made plausible by theoretical arguments alone. The aim of the present work is to provide direct experimental proof of the existence of three-body forces in an interacting system, specifically the existence of a three-spin interaction in the magnetic solid solution $CsMn_{0.28}Mg_{0.72}Br_3$, with use of the inelastic-neutron-scattering (INS) technique.

The exchange interaction of localized S-state ions is usually well approximated by the Heisenberg model which is based upon the bilinear spin permutation operator

$$P_{ij} = \tfrac{1}{2}(1 + \mathbf{S}_i \cdot \mathbf{S}_j). \quad (1)$$

An exact spin Hamiltonian will contain terms of higher order in the spin operators. nth-order exchange can formally be written as the product of n permutation operators; e.g., biquadratic exchange is thus of the form

$$P_{ij}^2 = \tfrac{1}{4}[1 + 2\mathbf{S}_i \cdot \mathbf{S}_j + (\mathbf{S}_i \cdot \mathbf{S}_j)^2], \quad (2a)$$

$$P_{ij}P_{jk} = \tfrac{1}{4}[1 + \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{S}_j \cdot \mathbf{S}_k + (\mathbf{S}_i \cdot \mathbf{S}_j)(\mathbf{S}_j \cdot \mathbf{S}_k)], \quad (2b)$$

$$P_{ij}P_{kl} = \tfrac{1}{4}[1 + \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{S}_k \cdot \mathbf{S}_l + (\mathbf{S}_i \cdot \mathbf{S}_j)(\mathbf{S}_k \cdot \mathbf{S}_l)]. \quad (2c)$$

The last terms on the right-hand side of Eqs. 2(a)–2(c) refer to two-spin, three-spin, and four-spin interactions, respectively. Recently we have demonstrated the importance of the biquadratic two-spin interaction, Eq. (2a), by an INS study of the excitation spectra of Mn^{2+} pairs in the solid solution $CsMn_xMg_{1-x}Br_3$.[5] We have now extended our measurements to include Mn^{2+} triads and found evidence for the existence of the biquadratic three-spin interaction, Eq. (2b), as discussed below.

$CsMnBr_3$ is a nearly ideal, isotropic, one-dimensional Heisenberg antiferromagnet with $S = \frac{5}{2}$. The exchange along the hexagonal c axis is almost 3 orders of magnitude larger than in other directions,[6,7] so that the formation of linear clusters of Mn^{2+} ions in $CsMn_xMg_{1-x}Br_3$ occurs along the c axis. The spin

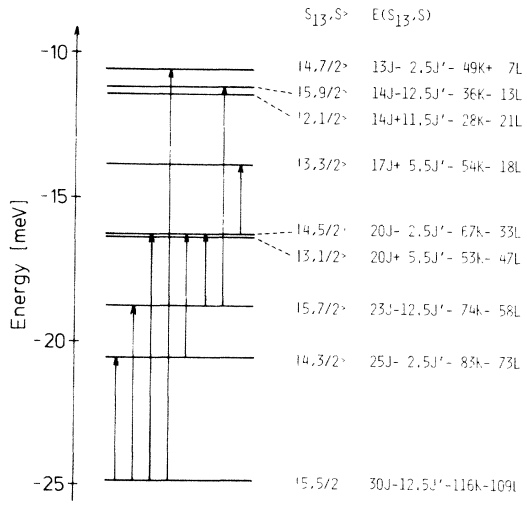

FIG. 1. Lower part of the energy-level scheme of Mn^{2+} triads in $CsMn_xMg_{1-x}Br_3$ calculated from the model parameters given in the text. The arrows denote the transitions observed in the present work.

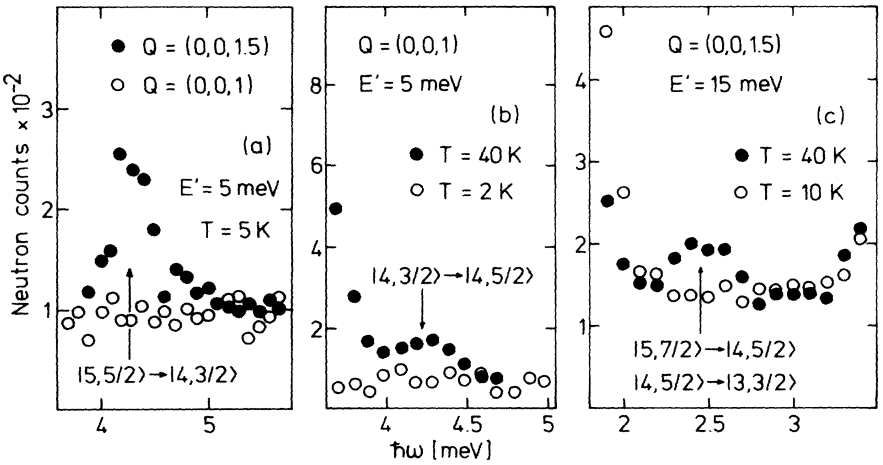

FIG. 2. Energy spectra of neutrons scattered from $CsMn_{0.28}Mg_{0.72}Br_3$. (a) The sideband at 4.8 meV corresponds to a longitudinal-optic phonon (Ref. 10). (b) The intensity increase at the low-energy side of the spectrum is due to an excited-state pair transition (Ref. 5). (c) The intensity increases at the low- and high-energy sides of the spectrum are caused by ground-state and excited-state pair transitions, respectively (Ref. 5). The (004) scattering planes were used for both the monochromator and the analyzer.

Hamiltonian of a Mn^{2+} triad in $CsMn_xMg_{1-x}Br_3$ with exchange couplings up to second order reads

$$\mathcal{H}=\mathcal{H}_1+\mathcal{H}_2+\mathcal{H}_3, \tag{3a}$$

with

$$\mathcal{H}_1=-2J(\mathbf{S}_1\cdot\mathbf{S}_2+\mathbf{S}_2\cdot\mathbf{S}_3)-2J'\mathbf{S}_1\cdot\mathbf{S}_3, \tag{3b}$$

$$\mathcal{H}_2=-K[(\mathbf{S}_1\cdot\mathbf{S}_2)^2+(\mathbf{S}_2\cdot\mathbf{S}_3)^2]-K'(\mathbf{S}_1\cdot\mathbf{S}_3)^2, \tag{3c}$$

$$\mathcal{H}_3=-L[(\mathbf{S}_1\cdot\mathbf{S}_2)(\mathbf{S}_2\cdot\mathbf{S}_3)+(\mathbf{S}_3\cdot\mathbf{S}_2)(\mathbf{S}_2\cdot\mathbf{S}_1)]. \tag{3d}$$

$\mathcal{H}_1$ and $\mathcal{H}_2$ describe the bilinear and biquadratic two-spin nearest- and next-nearest-neighbor exchange interactions, respectively, and $\mathcal{H}_3$ is equivalent to the biquadratic three-spin exchange coupling. Since $\mathcal{H}_2$ and $\mathcal{H}_3$ give rise to off-diagonal matrix elements, Eq. (3a) was diagonalized in first-order perturbation theory (i.e., for $|K|, |L| \ll |J|$). The low-energy part of the eigenvalues $E(S_{13},S)$ is illustrated in Fig. 1 for the model parameters resulting from the present experiments. The quantum number S denotes the total spin, $\mathbf{S}=\mathbf{S}_1+\mathbf{S}_2+\mathbf{S}_3$, and the additional quantum number S_{13} is given by $\mathbf{S}_{13}=\mathbf{S}_1+\mathbf{S}_3$. The eigenvalues $E(S_{13},S)$ are linear combinations of the model parameters which therefore can be directly determined by spectroscopic methods, e.g., by INS measurements.

In the INS experiment all transitions with $\Delta S=0, \pm1$ and $\Delta S_{13}=0, \pm1$ are allowed, and the intensity of a particular triad transition $|S_{13},S\rangle \rightarrow |S'_{13}, S'\rangle$ is given by[8]

$$\frac{d^2\sigma}{d\Omega\, d\omega}=\frac{2N}{3Z}\left(\frac{\gamma e^2}{m_e c^2}\right)^2\frac{k'}{k}\exp\{-2W(\mathbf{Q})\}F^2(\mathbf{Q})\sum_{\alpha,\beta}\left(\delta_{\alpha\beta}-\frac{Q_\alpha Q_\beta}{Q^2}\right)M^2_{\alpha\beta}\exp\left\{-\frac{E(S_{13},S)}{k_B T}\right\}$$

$$\times\{1+(-1)^{\Delta S_{13}}\cos(\mathbf{Q}\cdot\mathbf{R}_{13})+2\delta(S_{13},S'_{13})[1-\cos(\mathbf{Q}\cdot\mathbf{R}_{12})-\cos(\mathbf{Q}\cdot\mathbf{R}_{23})]\}. \tag{4}$$

N is the total number of triads in the sample, Z the partition function, k and k' the wave numbers of the incoming and scattered neutrons, respectively, $\mathbf{Q}=\mathbf{k}-\mathbf{k}'$ the scattering vector, $F(\mathbf{Q})$ the magnetic form factor, $M^2_{\alpha\beta}$ the transition probability, and $\mathbf{R}_{ij}=\mathbf{R}_i-\mathbf{R}_j$, where $\mathbf{R}_i$ is the position vector of the magnetic ion. The remaining symbols have their usual meaning.

The INS experiments were performed at the DR3 reactor at Risø and at the reactor Saphir at Würenlingen. At Risø the triple-axis spectrometer TAS7 which is installed at a neutron guide connected to a cold H_2 source, was used. The scattered neutron energy E' was held constant at 5 meV, giving rise to an energy resolution of 0.28 meV. At Würenlingen we used the triple-axis spectrometer R2 with either the incoming energy E or the outgoing energy E' of the neutron kept fixed at 15 meV. To gain intensity the experiments were carried out with use of a vertically or doubly bent graphite monochromator as well as a horizontally bent graphite analyzer, with the (002) planes

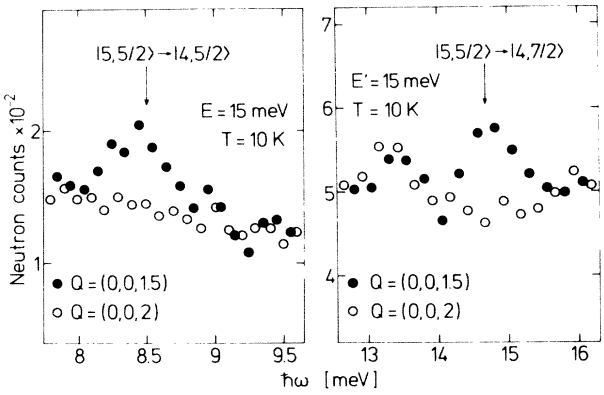

FIG. 3. Energy spectra of neutrons scattered from $CsMn_{0.28}Mg_{0.72}Br_3$.

as scattering planes for most scans. Pyrolitic graphite or cooled beryllium filters were inserted into the neutron beam to reduce higher-order contamination. The measurements were carried out in the neutron energy-loss configuration for several **Q** vectors in the temperature range $2 \leq T \leq 70$ K. The single crystal of $CsMn_{0.28}Mg_{0.72}Br_3$, grown by the Bridgman technique as a cylinder of 0.7-cm diameter and 1.5-cm length, was oriented so as to place the (101) plane into the scattering plane.

Typical energy spectra are shown in Figs. 2 and 3, which demonstrate the power of the INS technique to identify clearly the triad excitations according to the characteristic dependence of the peak intensities upon the scattering vector **Q** and the temperature T. The $|5,\frac{7}{2}\rangle \rightarrow |4,\frac{5}{2}\rangle$ and $|4,\frac{5}{2}\rangle \rightarrow |3,\frac{3}{2}\rangle$ triad transitions displayed in Fig. 2(c) could not be separated from each other, since they essentially coincide at the same energy and contribute to the scattering with roughly equal weight. Energy spectra of the $|5,\frac{5}{2}\rangle \rightarrow |5,\frac{7}{2}\rangle$ and $|5,\frac{7}{2}\rangle \rightarrow |5,\frac{9}{2}\rangle$ triad transitions have been published by Falk *et al.*[9] The phonon dispersion of $CsMn_{0.28}Mg_{0.72}Br_3$ has also been studied in detail[10] in order to avoid any misinterpretation of the observed spectra. Table I lists the eight excitations which have unambiguously been attributed to particular triad transitions according to the cross-section formula (4).

Various least-squares fitting procedures were used in the analysis of the experimental data as shown in Table I. Model A was based on the bilinear Heisenberg Hamiltonian [Eq. (3b)] and failed as expected.[5] The data analysis of model B was carried out on the basis of a two-spin Hamiltonian $\mathscr{H}_1 + \mathscr{H}_2$ [Eqs. (3b) and (3c)] with $K' = 0$, since $|J'| \ll |J|$ and therefore $|K'| \ll |K|$. The full Hamiltonian (3a) was used for model C (again with $K' = 0$), which provided a considerably improved standard deviation compared to model B. Thus the most reliable model parameters are

$$J = -0.777 \pm 0.006 \text{ meV},$$

$$K = (8.4 \pm 0.9) \times 10^{-3} \text{ meV},$$

$$J' = -0.011 \pm 0.009 \text{ meV},$$

$$L = (6.1 \pm 0.6) \times 10^{-3} \text{ meV}.$$

The nonzero value of L clearly demonstrates the existence of a three-spin interaction in $CsMn_{0.28}Mg_{0.72}Br_3$. Other types of interactions, in particular both single-ion or two-ion anisotropy terms and dipolar interactions, can

TABLE I. Observed and calculated triad transitions of Mn^{2+} ions in $CsMn_{0.28}Mg_{0.72}Br_3$, analyzed on the basis of the Hamiltonian (3) for $K' = 0$; (A) $J = -0.8702$ meV, $J' = -0.0083$ meV, $K = L = 0$; (B) $J = -0.7858$ meV, $J' = -0.0123$ meV, $K = 0.0143$ meV, $L = 0$; (C) $J = -0.7768$ meV, $J' = -0.0109$ meV, $K = 0.0084$ meV, $L = 0.0061$ meV. χ^2 denotes the standard deviation of the calculated transition energies from those measured.

$\lvert S_{13}S\rangle \rightarrow \lvert S'_{13},S'\rangle$	$E(S'_{13},S') - E(S_{13},S)$	$\hbar\omega_{obs}$ (meV)	$\hbar\omega_{calc}$ (meV) A ($\chi^2 = 5.22$)	B ($\chi^2 = 3.13$)	C ($\chi^2 = 1.67$)
$\lvert 5,\frac{5}{2}\rangle \rightarrow \lvert 4,\frac{3}{2}\rangle$	$-5J + 10J' + 33K + 36L$	4.27 ±0.03	4.27	4.27	4.27
$\lvert 5,\frac{5}{2}\rangle \rightarrow \lvert 5,\frac{7}{2}\rangle$	$-7J + 42K + 51L$	6.10 ±0.02	6.09	6.10	6.10
$\lvert 5,\frac{5}{2}\rangle \rightarrow \lvert 4,\frac{5}{2}\rangle$	$-10J + 10J' + 50K + 75L$	8.52 ±0.09	8.61	8.44	8.53
$\lvert 5,\frac{5}{2}\rangle \rightarrow \lvert 4,\frac{7}{2}\rangle$	$-17J + 10J' + 68K + 115L$	14.74 ±0.15	14.71	14.20	14.37
$\lvert 4,\frac{3}{2}\rangle \rightarrow \lvert 4,\frac{5}{2}\rangle$	$-5J + 16K + 40L$	4.21 ±0.08	4.35	4.16	4.26
$\lvert 5,\frac{7}{2}\rangle \rightarrow \lvert 4,\frac{5}{2}\rangle$	$-3J + 10J' + 8K + 25L$	2.45 ±0.10	2.53	2.34	2.44
$\lvert 5,\frac{7}{2}\rangle \rightarrow \lvert 5,\frac{9}{2}\rangle$	$-9J + 38K + 45L$	7.58 ±0.05	7.83	7.61	7.58
$\lvert 4,\frac{5}{2}\rangle \rightarrow \lvert 3,\frac{3}{2}\rangle$	$-3J + 8J' + 13K + 15L$	2.45 ±0.10	2.54	2.44	2.44

be ruled out, since the latter contribute less than 0.02 meV to the triad energies, and any anisotropic interaction would lift the $(2S+1)$-fold degeneracy of the spin multiplets, which is not observed. Intercluster interactions are expected to be smaller than $|J'|$ and thus not observable within the energy resolution of the present experiments; moreover they would broaden rather than shift the triad excitations.

As discussed in Ref. 5 it is likely that the biquadratic spin coupling of Mn^{2+} pairs in $CsMn_xMg_{1-x}Br_3$ is the result of magnetostrictive effects.[11] If this is also true for the triads, the biquadratic interaction will be of the form

$$\mathscr{H}_4 = -\tilde{K}(\mathbf{S}_1\cdot\mathbf{S}_2+\mathbf{S}_2\cdot\mathbf{S}_3)^2, \quad (5)$$

i.e., for $\tilde{K}=K=L$ and $K'=0$ we have $\mathscr{H}_4=\mathscr{H}_2+\mathscr{H}_3$, see Eqs. (3c) and (3d). Indeed, the biquadratic coupling parameters K and L resulting from our experiments are roughly equal, which supports the hypothesis of magnetostrictve forces being the origin of the biquadratic interaction.

In summary, we have demonstrated that biquadratic two-spin and particularly three-spin interactions distinctly contribute to the spin coupling of Mn^{2+} triads in $CsMn_xMg_{1-x}Br_3$. We point out that higher-order spin interactions usually cannot be unraveled by a study of the system in the cooperative state,[5] but manifest themselves only in especially tailored experiments as discussed above.

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