Origin of Higher Order Magnetic Exchange: Evidence for Local Dimer Exchange Striction in $\mathrm{CsMn_{0.28}Mg_{0.72}Br_3}$ Probed by Inelastic Neutron Scattering

Th. Strässle,* F. Juranyi, M. Schneider, S. Janssen, and A. Furrer
Laboratory for Neutron Scattering, ETH Zürich & PSI, 5232 Villigen PSI, Switzerland

K.W. Krämer and H. U. Güdel
Department of Chemistry and Biochemistry, University of Bern, 3012 Bern, Switzerland

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The origin of higher-order exchange interactions in localized S-state systems has been the subject of intensive investigations in the past. In particular, it has been suggested that a biquadratic exchange term may arise from the magnetoelastic energy. Here we report on the pressure and temperature dependence of the excitation spectra of magnetic $\mathrm{Mn^{2+}}$ dimers in $\mathrm{CsMn_{0.28}Mg_{0.72}Br_3}$ probed by inelastic neutron scattering. Biquadratic exchange and a strong distance dependence of the bilinear exchange are observed. It is shown that the mechanism of local exchange striction may explain the occurrence of biquadratic exchange in accordance with the elastic properties of the compound.

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The magnetic properties of a localized S-state system are commonly interpreted in terms of the Heisenberg model

$$\mathcal{H} = -2\sum_{i>j} J_{ij}\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j, \tag{1}$$

which inherently always represents a simplification of the true situation. Often on account of experimental findings higher-order exchange terms $K_{ij}(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j)^2$, $L_{ijl}(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j) \times (\hat{\mathbf{S}}_j \cdot \hat{\mathbf{S}}_l)$, etc., have to be added [1–5]. The physical origin of these terms, however, has been and still is the subject of serious discussions. In its simplest form the problem is represented by two isolated, exchange-coupled spins $\mathbf{S}_1$ and $\mathbf{S}_2$ forming a dimer:

$$\mathcal{H} = -2J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 - K(\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2)^2. \tag{2}$$

In the case of superexchange mediated interaction, the presence of intrinsic higher-order terms due to multielectron exchange has already been pointed out by Anderson [6]. However, other mechanisms equally resulting in higher-order exchange were proposed, including magnetic exchange striction, electric multipole interactions, the Jahn-Teller effect, and contributions of orbital anisotropy to exchange interactions (see, e.g., [7]). In the following we present data which give strong evidence for exchange striction being the major cause for the observed biquadratic exchange in $\mathrm{CsMn}_x\mathrm{Mg}_{1-x}\mathrm{Br}_3$ [8]. Exchange striction results from a geometrical degree of freedom which allows the two coupled ions to accommodate their distance in order to gain magnetic exchange energy at the expense of elastic energy [9]. Exchange striction is hence expected to be strong in systems with a pronounced distance dependence of the magnetic exchange and a soft host lattice. The magnetic quantity of higher-order exchange should thus be reflected in the local elastic properties between the two ions. Experimental evidence for the presence of exchange striction was given in earlier works [10–14]. The results are not conclusive due to the following reasons. First, some of the earlier works consider less isolated, complicated, exchange-coupled spin systems. Second, others are based on EPR and NMR measurements where the energy eigenvalues of Eq. (2) (and hence the presence of higher-order terms) must be indirectly determined from their thermal populations. Third, the distance dependence of the exchange is often taken from isostructural compounds despite the fact that the chemical substituents might add specific electronic properties. The data we present here are based on inelastic neutron spectroscopy (INS) which allow a direct measurement of the eigenvalues of Eq. (2) in the most direct way for expanded or reduced ion distances, which in turn are probed by neutron diffraction (ND) at the very same sample environment conditions. To our knowledge the present work constitutes the first investigation of this kind.

Formally, for a system of two isolated magnetic ions, which are coupled magnetically by bilinear exchange J and elastically by an effective, microscopic force constant f, exchange striction results from the minimization of the total energy W [10]:

$$\begin{aligned} W &= -2J(r)\mathbf{S}_1 \cdot \mathbf{S}_2 + \frac{f}{2}(\Delta r)^2 \\ &\simeq -2[J(r_0) + J'(r_0)\Delta r]\mathbf{S}_1 \cdot \mathbf{S}_2 + \frac{f}{2}(\Delta r)^2, \end{aligned} \tag{3}$$

where $J(r)$ is expanded up to first order around the equilibrium distance r_0 with $\Delta r = r - r_0$ and $J' = \partial J/\partial r$. The distance of minimal energy is obtained from

$$\frac{dW}{dr} = -2J'(r_0)\mathbf{S}_1 \cdot \mathbf{S}_2 + f\Delta r = 0, \tag{4}$$

resulting in

$$r_{\min} = r_0 + \frac{2J'(r_0)}{f}\mathbf{S}_1 \cdot \mathbf{S}_2. \tag{5}$$

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Substitution of $r_{\min} \to r$ back into Eq. (3) yields

$$W = -2J(r_0)\mathbf{S}_1 \cdot \mathbf{S}_2 - \frac{2[J'(r_0)]^2}{f}(\mathbf{S}_1 \cdot \mathbf{S}_2)^2. \qquad (6)$$

The second term in Eq. (6) may be directly associated with the biquadratic term in Eq. (2); thus the force constant f may be expressed in the magnetic properties J' and K:

$$f = \frac{2[J'(r_0)]^2}{K}. \qquad (7)$$

The ternary compound $CsMnBr_3$ is considered as a good approximation for a one-dimensional Heisenberg antiferromagnet (see [15] and references therein), which below the three-dimensional ordering temperature $T_N = 8.3$ K becomes a frustrated triangular antiferromagnet with striking ground-state properties (see [16,17] and references therein). It crystallizes in the hexagonal space group $P6_3/mmc$. Face-sharing $(MnBr_{6/2})$ octahedra form infinite chains along the c axis (Fig. 1) and are separated from each other by Cs^+ ions. The Mn^{2+} ions have a ^6S ground state with spin $S_i = 5/2$. The magnetic exchange J within the chain is about 3 orders of magnitude stronger than between the chains [15]. Random substitution of Mn^{2+} ions by nonmagnetic Mg^{2+} ions results in magnetic clusters via fragmentation of the Mn^{2+} chains, while leaving the lattice unchanged ($CsMnBr_3$ and $CsMgBr_3$ are isostructural and exhibit equal cell parameters within experimental accuracy). In the title compound $CsMn_{0.28}Mg_{0.72}Br_3$, the formation of dimers is a factor of 3.6 and 12.8 more frequent than the formation of trimers and tetramers, respectively [22]. No long-range magnetic order is observed down to at least 1.8 K. In a dimer, the coupling of the Mn spins results in six energy levels. Each is characterized by the total spin of the dimer $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ with $0 \leq S \leq 5$ and has a $(2S+1)$-fold degeneracy. Considering bilinear exchange only [Eq. (2), $K = 0$], the corresponding energy levels $E(S)$ must satisfy Landé's rule $E(S) - E(S-1) = -2SJ$ for $S > 0$. Dimer excitations of $CsMn_xMg_{1-x}Br_3$ have been studied earlier by INS [8,15]. However, the energy levels $E(S)$ were found to violate Landé's rule and could be explained only by including a biquadratic term such as in Eq. (2) [23]. Specifically, the parameters $J = -838(5)$ μeV and $K = 8.8(8)$ μeV were deduced [8,15]. In contrast to other spectroscopic methods, INS allows the simultaneous observation of several different dimer excitations $|S-1\rangle \to |S\rangle$. The energies of these excitations hence directly yield the energy eigenstates $|S\rangle$ and correspondingly the exchange parameters J and K from a single spectrum taken at a given temperature. This is a crucial point, as J exhibits a temperature dependence via the thermal expansion of the lattice as shown below. The temperature dependence of J might thus be interpreted erroneously as a violation of Landé's rule, if dimer excitations observed at different temperatures were compared. With the above values of J and K at hand, the microscopic force constant f may be estimated from microscopic magnetic properties, given that the distance dependence J' of the bilinear exchange is known [Eq. (7)]. The resulting value of f can then be compared to elastic properties of $CsMn_xMg_{1-x}Br_3$.

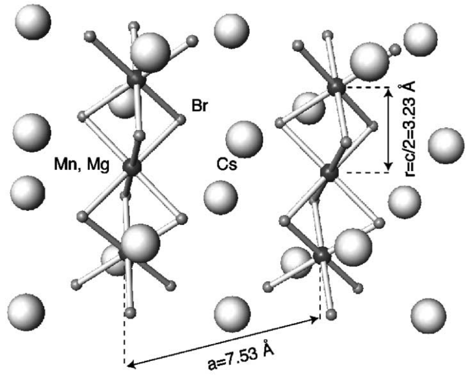

FIG. 1. Crystal structure of $CsMn_xMg_{1-x}Br_3$: the $[(Mn, Mg)Br_{6/2}]$ octahedra form chains along the c axis well separated by Cs^+ ions.

Polycrystalline $CsMn_{0.28}Mg_{0.72}Br_3$ was prepared according to standard procedures [15]. The INS measurements were performed on the time-of-flight spectrometer FOCUS at the spallation neutron source SINQ of PSI in Switzerland with an incoming neutron energy of 7.1 meV in neutron energy loss configuration. The ND measurements were carried out on the high resolution powder diffractometer HRPT at SINQ. The measurements under pressure were done in an axial-symmetric pressure cell made of hardened aluminum with a total sample volume of $\sim$1600 mm^3 [18]. Fluorinert was used as the pressure transmitting medium. The pressure was determined at base temperature by the shift in the lattice parameter of NaCl [19] added to the sample. The INS measurements under pressure were carried out right after the ND measurements under pressure in the very same sample environment.

Figure 2 shows inelastic neutron spectra of $CsMn_{0.28}Mg_{0.72}Br_3$ measured at ambient pressure for different temperatures T and spectra at elevated pressure for $T = 50$ K. The strongest peaks are ascribed to the three first dimer excitations $|\mathbf{S}-1\rangle \to |\mathbf{S}\rangle$. The weaker peaks at around 4 meV are due to n-mer excitations with $n > 2$. All peaks can readily be fitted by Gaussians with widths essentially defined by the instrumental resolution. To account for the weaker statistics of the measurements in the pressure cell [Figs. 2, (*e*) and (*f*)], the widths of the respective peaks were fixed to values calculated from the resolution function of the instrument. In this way the first dimer excitation (near 2 meV) is better distinguished from the large elastic peak due to the pressure cell. The resulting peak positions yield directly the bilinear and biquadratic exchange parameters via [from Eq. (2)]

$$\Delta E(|\mathbf{S}-1\rangle \to |\mathbf{S}\rangle) = -2S[J + K(2S^2 - 35)]. \qquad (8)$$

Together with the lattice parameters c determined from

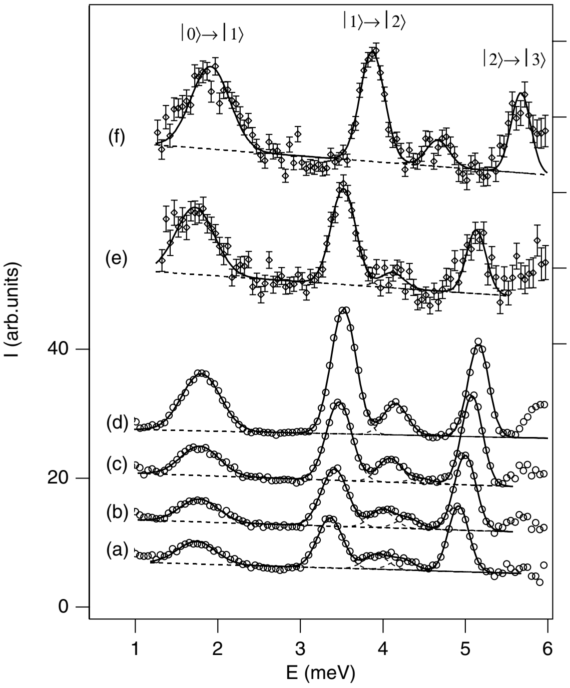

FIG. 2. Inelastic neutron spectra of the three first dimer excitations $|\mathbf{S}-1\rangle \rightarrow |\mathbf{S}\rangle$ in $\mathrm{CsMn_{0.28}Mg_{0.72}Br_3}$: (*a*)–(*d*) measurements without pressure cell, $P = 0$, $T = 200, 150, 100, 50$ K; (*e*) and (*f*) measurements in the pressure cell at $T = 50$ K and $P = 0, 0.52(5)$ GPa. The intensity at around 4 meV is due to excitations from n-mers with $n > 2$. Lines refer to Gaussian peak fits.

the ND measurements, we find the dependence of J and K on the intradimer distance $r = c/2$ as shown in Fig. 3 and listed in Table I. Apparently, $J(r)$ varies considerably for a distance change of a few 1/100 Å, whereas $K(r)$ essentially remains constant. Bearing in mind that the observed effective exchange between the two ions likely results from a superposition of different exchange pathways, we empirically parametrize $J(r)$ by a second order polynomial and $K(r)$ by a straight line (solid lines in Fig. 3). The observed distance dependence of $J(r)$ confirms our earlier measurements under pressure [20] (stars in Fig. 3), which considered only the first dimer excitation $|0\rangle \rightarrow |1\rangle$ and, hence, for the sake of consistency, have been excluded in parametrizing $J(r)$.

At $T \sim 50$ K and $P = 0$ we find $J' = 3.6(3)$ meV/Å and $K = 8.6(2)$ μeV and obtain from Eq. (7):

$$f = 3.1(6)\ \mathrm{eV/Å^2} = 50 \pm 10\ \mathrm{N/m}.$$

This value for the *local* effective force constant between the two dimer ions may now be compared with the elastic properties of the compound. The phonon spectrum of $\mathrm{CsMn_{0.28}Mg_{0.72}Br_3}$ has not been completely established from INS and hence f cannot be determined directly from an atomic force model. Thus macroscopic elastic constants of the isostructural compound $\mathrm{CsNiF_3}$ are used to estimate the order of magnitude of f. These elastic constants were determined by INS measurements of the phonon spectrum of $\mathrm{CsNiF_3}$. They reveal that the chains of $\mathrm{NiF_6}$ octahedra form rigid rods [21] with a small elastic coupling between each other. With the Cs atoms acting as a soft sublattice, the force constant f is expected to be roughly proportional to the macroscopic elastic constant c_{33} along the c axis. The two constants are linked to each other via the elastic energy density, which for hexagonal symmetry reads

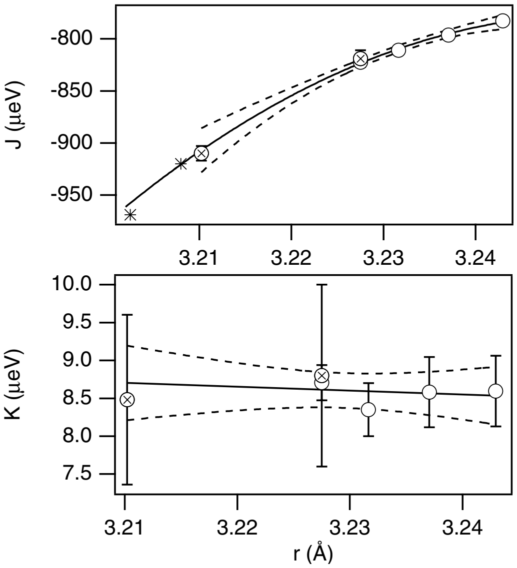

FIG. 3. Dependences of the bilinear and biquadratic exchange parameter (J and K) on the intradimer distance r (crossed circles: $P = 0, 0.52(5)$ GPa at $T = 50$ K, in pressure cell; empty circles: ambient pressure at $T = 50, 100, 150, 200$ K). Solid lines refer to polynomial fits (see the text) with the dashed lines their respective confidence bands (95%). Stars represent results from earlier measurements under pressure [$P = 0.56(2), 0.73(2)$ GPa at $T = 4.2$ K] not considered for the fit (see the text and Table I).

$$u_{\mathrm{el}} = \tfrac{1}{2}c_{11}(e_{xx}^2 + e_{yy}^2) + \tfrac{1}{2}c_{33}e_{zz}^2 + c_{13}(e_{xx}e_{zz} + e_{yy}e_{zz}) + c_{12}e_{xx}e_{yy}. \quad (9)$$

If the rods are responsible for the stiffness along c, one may set $e_{xx} = e_{yy} = 0$ and consider only a *local,* longitudinal distortion of the unit cell $e_{zz} = (\Delta r)^2/r_0^2 \neq 0$. The associated energy per dimer which occupies half of the unit cell ($V = \sqrt{3}a^2c/2$, $r_0 = c/2$) is

$$W_{\mathrm{el}} = \frac{V}{2}u_{\mathrm{el}} = \frac{\sqrt{3}}{4}a^2c\frac{c_{33}}{2}\left(\frac{\Delta r}{r_0}\right)^2. \quad (10)$$

A comparison of this energy with the second term of Eq. (3) yields the effective force constant

$$f = \sqrt{3}c_{33}\frac{a^2}{c}. \quad (11)$$

With $a = 7.5304$ Å, $c = 6.4516$ Å, and $c_{33} = 64$ GPa, where the latter value is taken from $\mathrm{CsNiF_3}$ [21], one finds $f \sim 100$ N/m. In ionic crystals the acoustic phonon frequencies scale as $\omega \sim (c\sqrt{M})^{-1}$ with M the molar mass and c the lattice parameter. A corresponding scaling

TABLE I. Intradimer distance, bilinear and biquadratic exchange parameters, and excitation energies of $CsMn_{0.28}Mg_{0.72}Br_3$ measured at different temperatures and pressures (values at $T = 4.2$ K from earlier measurements [20] of the $|0\rangle \rightarrow |1\rangle$ excitation only, with $K = 8.8$ μeV assumed to be constant).

T (K)	P (GPa)	r (Å)	J (μeV)	K (μeV)	$E_{|0\rangle\rightarrow|1\rangle}$ (meV)	$E_{|1\rangle\rightarrow|2\rangle}$ (meV)	$E_{|2\rangle\rightarrow|3\rangle}$ (meV)
200	0	3.2429(1)	−783(2)	8.60(47)	1.741(13)	3.361(4)	4.917(4)
150	0	3.2371(1)	−796(2)	8.58(47)	1.771(12)	3.414(4)	4.998(4)
100	0	3.2316(1)	−811(2)	8.35(35)	1.781(9)	3.468(3)	5.080(3)
50	0	3.2275(1)	−823(1)	8.71(23)	1.798(4)	3.524(2)	5.158(3)
50	0.52(5)	3.210(1)	−910(7)	8.5 ± 1.1	1.957(7)	3.872(8)	5.672(18)
4.2	0.56(2)	3.208(2)	−920(2)		1.981(8)		
4.2	0.73(2)	3.101(1)	−969(2)		2.079(4)		

of c_{33} [24] thus yields for $CsMn_{0.28}Mg_{0.72}Br_3$ an extrapolated effective force constant of $f \sim 54$ N/m [Eq. (11)]. The good agreement between f deduced from the magnetic quantities (J', K) and deduced via the macroscopic elastic properties shows that aside local-exchange striction other mechanisms sparsely contribute to the observed biquadratic exchange in $CsMn_{0.28}Mg_{0.72}Br_3$. In fact, the Jahn-Teller effect and orbital anisotropy are altogether excluded for Mn^{2+} ions, whereas contributions from multielectron exchange and multipole interactions are hard to estimate. Even their signs are not sure [6].

The value of the effective elastic force constant f of a magnetic dimer in $CsMn_{0.28}Mg_{0.72}Br_3$ was deduced in two ways: (i) from microscopic, purely magnetic quantities ($J' = \partial J/\partial r$ and K) subject to local exchange striction and (ii) from macroscopic elastic constants. Considering the approximations made in the derivations, the two values are in fair agreement. The two basic requirements for local exchange striction are fulfilled in $CsMn_xMg_{1-x}Br_3$, namely, (i) a strong distance dependence of the exchange and (ii) a soft host lattice, which allows the two ions to accommodate their distance locally. We therefore conclude that the presence of biquadratic exchange in $CsMn_{0.28}Mg_{0.72}Br_3$ is caused, at least to a major extent, by the mechanism of exchange striction.

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*Present address: Physique des Milieux Condensés, Université Pierre et Marie Curie B77, 4 Place Jussieu, 75252 Paris, France.
Electronic address: ts@pmc.jussieu.fr

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[22] The number of n-mers per total number of (Mn + Mg) atoms is $P(x, n) = x^n(1 - x)^2$.
[23] Dipolar interaction can be ruled out to have a detectable effect on the violation of Landé's rule in $CsMn_{0.28}Mg_{0.72}Br_3$. With a dipolar coupling parameter of 3.2 μeV, the variation of the intradimer distance induced by P and T results in a change of the dipolar coupling strength by ≈ 0.15 μeV with corresponding changes of the dimer splittings of 0.3, 0.6, and 0.9 μeV, i.e., within experimental errors (Table I).
[24] $c_{33} = \rho v_{33}^2 \sim \frac{M}{V}(\frac{\partial \omega}{\partial k})^2 \sim \frac{1}{V}$ with density ρ, longitudinal sound velocity v_{33} along the c axis, wave vector k, and volume V.