RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 28, NUMBER 9 1 NOVEMBER 1983

Collective excitations in the singlet-ground-state dimer system $Cs_3Cr_2Br_9$

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(Received 23 May 1983)

Inelastic-neutron-scattering experiments have been performed on a novel singlet-ground-state system with isotropic spin-only states consisting of Cr^{3+} dimers. The results are well described with the use of a simple Heisenberg model and with only nearest-neighbor interactions being considered.

Singlet-ground-state magnetism has attracted much attention especially for systems with a near critical ratio of the interaction strength, which favors magnetic ordering, and the energy splitting, which isolates the nonmagnetic ground state.[1] Here we present the first measurements on a novel kind of singlet-ground-state system, namely, the insulator $Cs_3Cr_2Br_9$ which possesses spin-only dimerized states.[2] This is in contrast to the rare-earth systems[3] which have been investigated so far and where the electronic states still have a strong anisotropy due to the admixture of orbital wave functions. Thus the dynamics of this spin system is much simpler, and, as it turns out, it can satisfactorily be described by a random-phase-approximation (RPA) calculation, considering nearest-neighbor interactions only.

The experiments were performed on a single crystal of $Cs_3Cr_2Br_9$, which exemplifies the family of compounds where the trivalent transition-metal ions are strongly coupled pairwise to form magnetic dimers in $Cr_2Br_9^{3-}$ complexes.[2] The crystal structure is hexagonal, space group $P6_3/mmc$ (D_{4h}^6), with two dimers per unit cell forming two sublattices. The dimers are oriented along the trigonal axis. The Cr-Cr separation is 3.3 Å within the dimers, and 7.4 (same sublattice) and 7.5 Å (different sublattices) between nearest-neighbor dimers. Figure 1 shows a schematic drawing of the structure, indicating the couplings which act not only within the dimers (J) but also between dimers (J_p,J_c), as will be discussed later. From low-temperature magnetic and spectroscopic measurements it was concluded that the coupling between the two $S=\frac{3}{2}$ Cr^{3+} ions of one dimer is antiferromagnetic which leads to an $S=0$ ground state followed by the $S=1$, $S=2$, and $S=3$ excited states.

The energy separation between the $S=1$ and the higher dimer states is large compared with the temperatures used (between 1.6 and 10 K) so that we can focus attention only on the two lower states, which can be regarded as an isotropic ($S=0$)-($S=1$) singlet-triplet system arising from coupled ions with effective spin $\frac{1}{2}$.

The magnetic dipole transitions between these two states are investigated by inelastic neutron scattering. The experiments were performed on the triplet-axis spectrometer TAS-7 which is located at the cold source of the DR3 reactor at Risø National Laboratory. The final energy was fixed to 5 meV during the experiments and the neutron beam was typically collimated to 60′-40′-40′-40′. In order to remove higher-order contamination a 10-cm-long, cooled Be filter was placed before the analyzer. Figure 2 shows some examples of neutron spectra that showed well-defined inelastic transitions. At 1.6 K we measured the dispersion in three different directions in the Brillouin zone. The results are presented in Fig. 3. The Γ–A direction points along the trigonal axis ($\langle 001 \rangle$ direction). Two other directions in the basal plane are indicated by Γ–K ($\langle 110 \rangle$) and by Γ–M ($\langle 100 \rangle$). Two excitations exist for each momentum transfer corresponding to the optic and acoustic mode. The solid lines in the figure are the calculated dispersion curves.

Near the K point at which the two modes are degenerate by symmetry the dispersion curves exhibit pronounced minima. A study of the temperature dependence near these minima showed typical soft-mode behavior although the softening is not complete. This indicates that no magnetic order occurs in this compound above 1.5 K, whereas ordering at lower temperatures due to interactions[4] that are not included in the theoretical model discussed below cannot be excluded.

The excitation spectrum can be calculated with the Hamil-

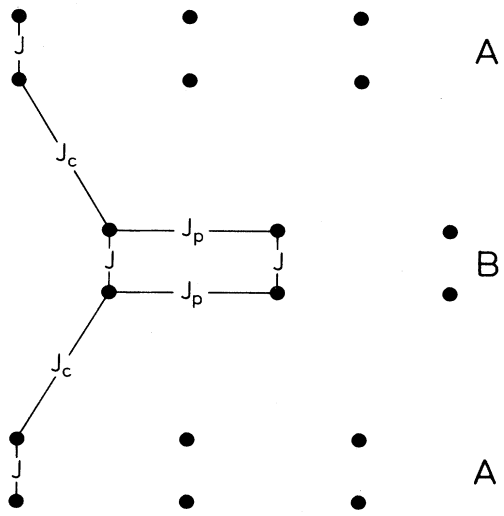

FIG. 1. Schematic drawing of the structure of $Cs_3Cr_2Br_9$ where the dots represent the Cr^{3+} ions. The other ions are not given. The interaction between the Cr ions is expressed by the arrows which are labeled by the coupling constants J, J_p, and J_c. A and B indicate the two sublattices.

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$$H = H_0 + H_1 = -J \sum_i \vec{S}_{i1} \cdot \vec{S}_{i2} - \left(J_p \sum_{i,j} (\vec{S}_{i1} \cdot \vec{S}_{j1} + \vec{S}_{i2} \cdot \vec{S}_{j2}) + J_c \sum_{i,j'} (\vec{S}_{i1} \cdot \vec{S}_{j'2} + \vec{S}_{i2} \cdot \vec{S}_{j'1}) \right) . \quad (1)$$

J is the intradimer exchange, while J_p and J_c are the exchange within and between the sublattices, respectively (see Fig. 1). As the exchange within one dimer is stronger than the coupling between Cr^{3+} ions of different dimers we first diagonalized H_0 and then solved the whole Hamiltonian by the conventional Green's-function method.[5] The result for the dispersion relation is

$$\begin{Bmatrix} \omega^{ac}(\vec{q}) \\ \omega^{opt}(\vec{q}) \end{Bmatrix} = \{J^2 + 2M^2(n_0 - n_1)J[J_p\gamma_p(\vec{q}) \mp J_c|\gamma_c(\vec{q})|]\}^{1/2} \quad (2)$$

for the optic and acoustic mode corresponding to the plus and minus sign, respectively; $M^2 = 5$ is the square of the transition matrix element between the ground state and first excited state. Both states are occupied according to the population factors n_0 and n_1; $\gamma_p(\vec{q})$ and $\gamma_c(\vec{q})$ are the Fourier sums over nearest neighbors within and between the sublattices. A fit to the measured excitations at $T = 1.6$ K neglecting renormalization effects yields $J = -1.01$ meV, $J_p = -0.028$ meV, and $J_c = -0.020$ meV. This shows the strong antiferromagnetic intradimer coupling, and the interdimer couplings, which are also antiferromagnetic and two orders of magnitude weaker. Although these constants are merely fitting parameters the different values for J_p and J_c may reflect the different exchange paths for the superexchange between the Cr^{3+} ions on nearest-neighbor dimers. Using these parameters one obtains

$$\frac{|2M^2J^*|}{J} = 0.97 ,$$

where

$$J^* = J_p\gamma_p(\vec{q}_0) - J_c|\gamma_c(\vec{q}_0)|$$

at the minimum of the dispersion $\omega(\vec{q}_0)$. This shows that the system is a slightly undercritical Van Vleck magnet close to the formation of spontaneous magnetization.

The scattering law is given by

$$\frac{d^2\sigma}{d\Omega\, d\omega} \sim F^2(\vec{\kappa}) M^2 [1 - \exp(-\beta\omega)]^{-1} (n_0 - n_1)(1 - \cos\vec{\kappa} \cdot \vec{R}) \times \left([1 + \cos(\vec{\rho} \cdot \vec{\tau} + \phi)] \frac{1}{\omega^{ac}} \delta(\omega - \omega^{ac}) + [1 - \cos(\vec{\rho} \cdot \vec{\tau} + \phi)] \frac{1}{\omega^{opt}} \delta(\omega - \omega^{opt}) \right) , \quad (3)$$

where $\beta = \hbar/k_B T$, $F^2(\vec{\kappa})$ is the square of the form factor of the Cr^{3+} ions, $\vec{\kappa} = \vec{\tau} + \vec{q}$ is the momentum transfer, τ is a reciprocal-lattice vector, $\vec{\rho}$ is a vector connecting the two sublattices, and $\vec{R}$ connects the two Cr^{3+} ions in a dimer. The term $F^2(\vec{\kappa})(1 - \cos\vec{\kappa} \cdot \vec{R})$ gives the form factor of the dimer for the singlet-triplet transition.[6] The resonances in the scattering law are given by the δ functions, which are weighted by the structure factors $[1 \pm (\cos\vec{\rho} \cdot \vec{\tau} + \phi)]$ for the acoustic and optic mode, respectively; ϕ is the phase of γ_c. Thus we are able to distinguish between the optic and the acoustic excitation in our experimental neutron spectra

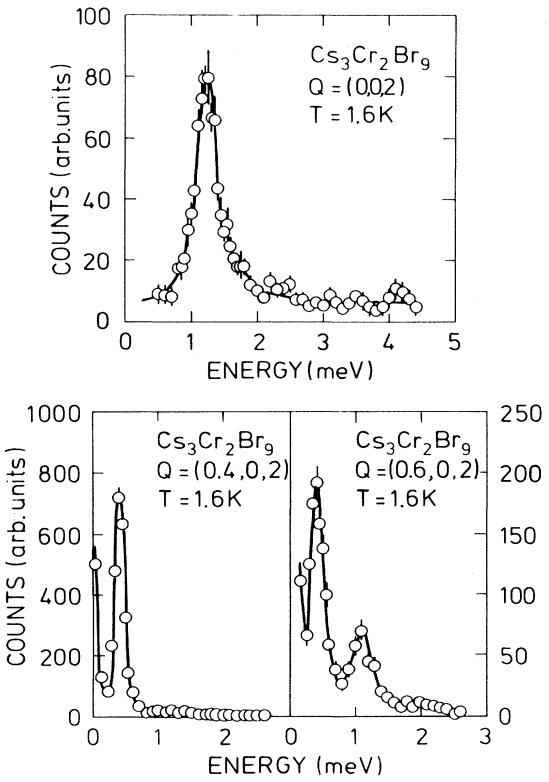

FIG. 2. Some examples of neutron spectra exemplifying the well-defined singlet-triplet transitions in $Cs_3Cr_2Br_9$.

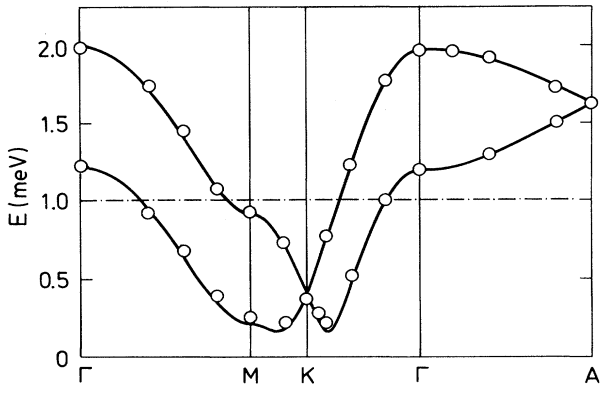

FIG. 3. Dispersion relation along three different directions in the reciprocal lattice as discussed in the text. The upper branch is the optic mode, the lower one the acoustic. The full lines are the calculated dispersion. The dotted horizontal line corresponds to J.

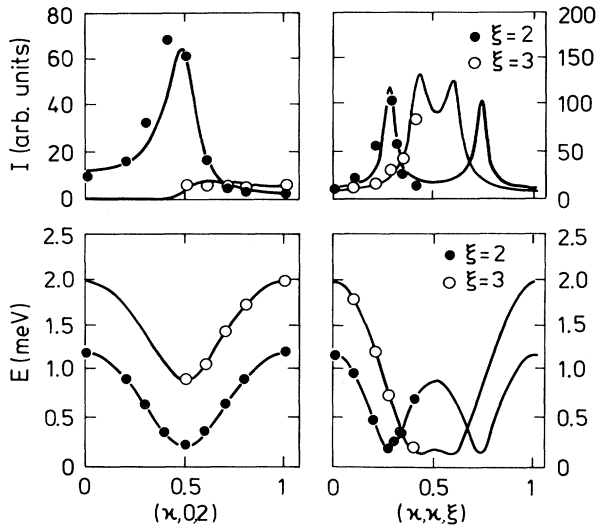

FIG. 4. Intensity of the excitations is given in the upper part of the figure for different scans through the reciprocal lattice. The corresponding dispersion curves are repeated below.

by their different intensities in different parts of the reciprocal lattice. This is shown in Fig. 4 where we have plotted the relative intensities of the two branches along different directions in the reciprocal lattice. The excellent agreement between theory and experiment is obvious.

An interesting feature becomes visible if one plots the contours of constant energy of the acoustic branch of the dispersion as given in Fig. 5, as has been done for $RbFeCl_3$.[4] The shaded part shows the flat part of the dispersion between two $\hbar\omega = 0.2$ meV contours. The absolute minimum within this area was calculated numerically and showed an exact degeneracy along one closed line. Thus the infinite number of equivalent points on this line leads to frustration and to no magnetic order of the dimers within the chosen model.

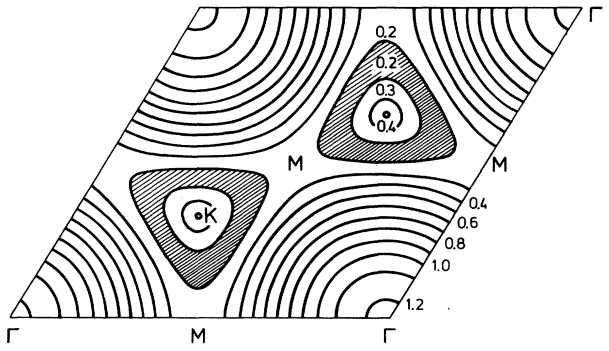

FIG. 5. Contour plot in the basal plane of the dispersion of the acoustic mode. The shaded part gives the area of possible ordering wave vectors showing the large frustration of the system.

An interesting aspect of this system would be how it behaves with an applied magnetic field which will raise the degeneracy of the triplet and probably will push the excitations on that line to zero energy. These experiments are now underway.

ACKNOWLEDGMENTS

We would like to acknowledge many helpful discussions with P.-A. Lindgård, P. Bak, and J. Jensen. The $Cs_3Cr_2Br_9$ crystal was prepared by A. Stebler. This work was partially supported by the Swiss National Science Foundation.

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