Molecular Spin Resonance in the Geometrically Frustrated Magnet $MgCr_2O_4$ by Inelastic Neutron Scattering

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We measured two magnetic modes with finite and discrete energies in an antiferromagnetic ordered phase of a geometrically frustrated magnet $MgCr_2O_4$ by single-crystal inelastic neutron scattering, and clarified the spatial spin correlations of the two levels: one is an antiferromagnetic hexamer and the other is an antiferromagnetic heptamer. Since these correlation types are emblematic of quasielastic scattering with geometric frustration, our results indicate instantaneous suppression of lattice distortion in an ordered phase by spin-lattice coupling, probably also supported by orbital and charge. The common features in the two levels, intermolecular independence and discreteness of energy, suggest that the spin molecules are interpreted as quasiparticles (elementary excitations with energy quantum) of highly frustrated spins, in analogy with the Fermi liquid approximation.

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The concept of geometric frustration was first pointed out by Wannier in 1950 for the classic spin systems in the two-dimensional triangular lattice [1], and has attracted much interest as a paradigm to bring out a novel paramagnetic state. In a geometrically frustrated magnet, the approximation of classic spin with only freedom of direction can be broken down, because the special atomic arrangement, based on a triangle and a tetrahedron, gives rise to an inherent macroscopic ground-state degeneracy in the classic ground state [1,2]. Therefore, magnetic quasielastic scattering in the paramagnetic phases was intensively studied by neutron scattering in spinel, pyrochlore, kagome, triangular systems, and so on. As a result, characteristic spatial correlations of spins were found, such as a small six-spin cluster [3–8], a large six-spin cluster [9], a seven-spin cluster [10], spin ice [11,12], and short-range order with propagation vector(s) [13,14].

On the other hand, in a magnetically ordered phase, geometric frustration is supposed to vanish due to the lattice distortion. Therefore, few neutron studies on spin fluctuations have been performed in an antiferromagnetic phase. Among them, two powder inelastic scattering studies discovered novel spin-excitation modes with discrete energies (spin resonance levels), two modes of $E = 4.5$ and 9.0 meV in a spinel $ZnCr_2O_4$ [15] and the similar first level at around $E = 4.5$ meV in a spinel $MgCr_2O_4$ [6], where E is energy. However, no information on the spatial spin correlations was obtained by these experiments on powder samples.

The B sites in the spinel AB_2O_4 construct corner-sharing tetrahedra, in which a plane of corner-sharing triangles (kagome lattice) and a plane of triangular lattice are alternatively stacked along the [111] direction, an excellent stage for geometric frustration. The two spinels, consisting of the magnetic ions of Cr^{3+} ($S = 3/2$) at only the B sites, undergo a first order transition from a cubic paramagnetic phase to a tetragonal antiferromagnetic phase at Nèel temperature $T_N \simeq 13$ K, and exhibit close values of Curie-Weiss temperature, $\theta_W = -370$ and -390 K [15–18]. The spin systems are almost equivalent in the two chromites, and are well known as the prototype of geometric frustration.

Figures 1(a) and 1(b) show our inelastic neutron scattering data on a powder specimen of $MgCr_2O_4$ in the antiferromagnetic phase. Since the earlier measurement on the same system [6] did not measure the second level, we extended the energy range and confirmed the second mode. The two discrete levels are observed around $E = 4.5$ and 9.0 meV, as shown in Figs. 1(a) and 1(b). Meanwhile, the paramagnetic phase exhibits magnetic quasielastic scattering around $Q = 1.5$ Å^{-1} shown in Fig. 1(c), where Q is the absolute value of a scattering vector, of which the spatial correlation was identified to be independent antiferromagnetic six-spin clusters (hexamers) by single-crystal specimens [3,6]. Then one of the challenging issues

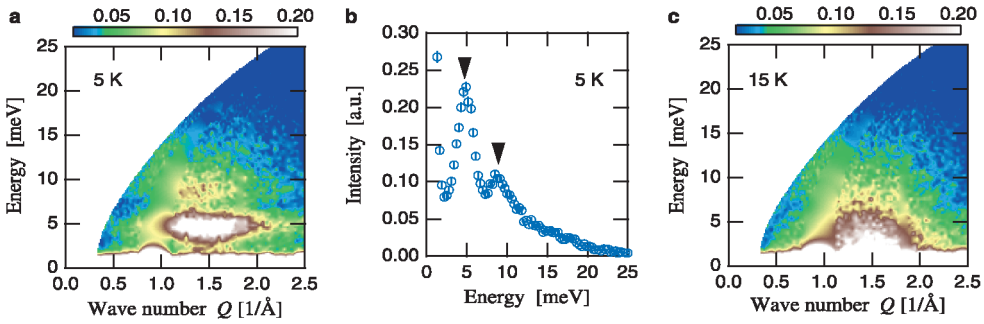

FIG. 1 (color). (a),(c) Color images of experimental data of inelastic magnetic scattering in the Q and E space on a powder specimen of $MgCr_2O_4$. The color gauges indicate the scattering intensity in arbitrary units. (b) Energy spectra, integrated from 17 to 28 deg in scattering angle, corresponding to the position around $Q = 1.5$ Å^{-1} in elastic condition.

in this system is to solve the spatial spin correlation of each discrete mode. In order to clarify this issue, we performed *inelastic* neutron scattering experiments on a *single-crystal* specimen of $MgCr_2O_4$ in the ordered phase. The results demonstrate that the effect of geometric frustration is clearly observed in the dynamical spin spatial correlation irrespective of small lattice distortion in the ordered phase.

Neutron scattering experiments on a single-crystal specimen were performed on a triple axis spectrometer HER, installed at a cold guide tube of the JRR-3M reactor, and on triple axis spectrometers PONTA and TOPAN, installed at the same reactor, Japan Atomic Energy Agency (JAEA), Tokai, Japan. The energy of the final neutrons was fixed at 3.0, 15, and 14 meV, respectively. A cooled Be filter or a pyrolytic graphite filter efficiently eliminated the higher order contamination. In the HER and PONTA experiments, horizontal focusing analyzers were used to merge the intensities in ranges of about 7 and 3 degrees scattering of angle, respectively. The single crystals of $MgCr_2O_4$ were grown by the flux method. A specimen of several single crystals with total mass over 300 mg, comounted on another triple axis spectrometer AKANE, was enclosed with He exchange gas in an aluminum container, which was set under the cold head of a closed-cycle He refrigerator. Neutron scattering experiments on a powder specimen were performed on a direct geometry chopper spectrometer INC, installed at the spallation neutron source, KENS, High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The energy of the incident neutrons was fixed at 30 meV. A 50 g powder specimen of $MgCr_2O_4$ was synthesized by the solid reaction method, shaped to an area by 50×50 mm^2 and enclosed and sealed similarly to the single-crystal assembly.

Figures 2(a) and 2(b) are the constant-energy scan data in the $hk0$ zone and the hhl zone, respectively. These data show the first resonance at $E = 4.5$ meV and $T = 6$ K (antiferromagnetic phase), where T is temperature. Surprisingly, the first resonance exhibits the same patterns as the paramagnetic quasielastic scattering in the earlier single-crystal data [3,6]. The magnetic diffuse scattering appears along the boundary of the 220 Brillouin zone in Fig. 2(a) and around 5/4 5/4 0 and 3/4 3/4 2 in Fig. 2(b). Such patterns of scattering intensity are reproduced by the model of hexamers in the kagome lattice perpendicular to the [111] direction, shown in Fig. 2(i) [3]. The square of the form factor of the hexamer is calculated by the relation

$$|F(\boldsymbol{Q})|^2 = \left\langle \left| \sum_{m=1}^{N} S_m \exp(i\boldsymbol{Q} \cdot \boldsymbol{r}_m) \right|^2 \right\rangle, \qquad (1)$$

where F is the form factor of a spin molecule, $\boldsymbol{Q}$ is a scattering vector, S_m is equal to ± 1 (relative spin correlation dynamically fluctuating in arbitrary directions), $\boldsymbol{r}_m$ is a position vector of the spin site m, N is the number of vertices of the shape (here 6), and $\langle\ \rangle$ means the orientation average over the eight $\langle 111 \rangle$ directions [3]. Multiplying the square of the Watson-Freeman form factor of Cr^{3+} ion, we obtain the patterns of Figs. 2(e) and 2(f) [19], that are in an excellent agreement with those of Figs. 2(a) and 2(b).

Figures 2(c) and 2(d) show the data of the second resonance on the $hk0$ zone and the hhl zone, respectively, measured in the constant-energy scan at $E = 9.0$ meV. Relatively strong signals are observed around 200 and 020, and a relatively weak one is somewhat distributed around 7/4 7/4 0 in Fig. 2(c). The diluted scattering intensity spreads out so as to connect these three points. In Fig. 2(d), magnetic scattering is relatively strong around 002, and is distributed through 111 towards 3/2 3/2 0. The scattering pattern in Fig. 2(d) looks alike that of the independent seven-spin clusters (heptamers), proposed in the pyrochlore material $Tb_2Ti_2O_7$ with the isomorphic magnetic lattice as the B sites in a spinel material, though only the hhl zone was studied in the Tb compound [10,20]. The heptamer consists of two face-to-face triangles in the two kagome lattices and the sandwiched point in the triangular lattice, as shown in Fig. 2(j). We also remark that the same structural unit was recently discussed in the spinel AlV_2O_4, though the spin correlation is unresolved by neutron scattering [21]. The spin correlation model of $Tb_2Ti_2O_7$ is explained as follows. All the spins alternatively align on the lines along the [110] and $[1\bar{1}0]$ directions, described by the bold blue lines. Fixing the direction of the three spins on the centered line, there are the four types of combinations coming from the remaining two lines, as shown in

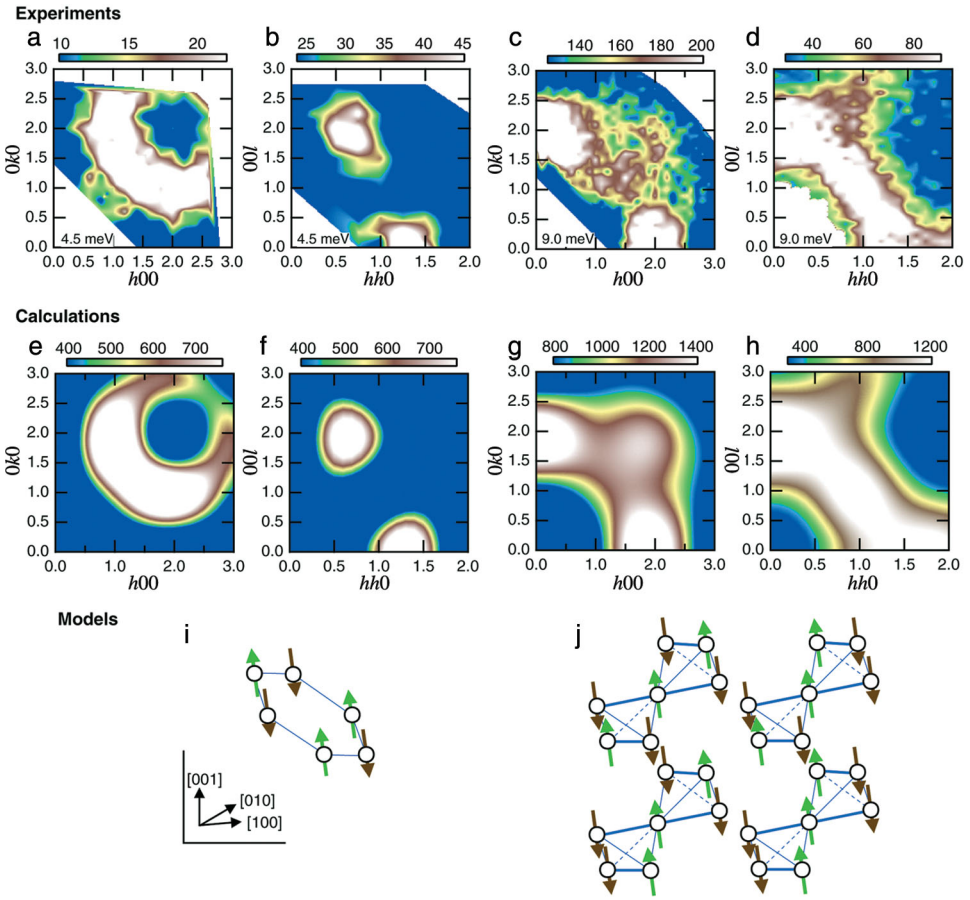

FIG. 2 (color). Color images of single-crystal inelastic scattering data of $MgCr_2O_4$, measured in a constant-energy mode. The horizontal gauges indicate the scattering intensity in arbitrary units. (a) and (b) The maps of experimental intensity, measured at 4.5 meV at 6 K in the $hk0$ zone and the hhl zone on HER, respectively. We also confirmed the same patterns at 1 meV at 15 K. In (a), the area above the [110] line was measured, and that below the line is folded to save beam time. (c) and (d) show the maps, measured at 9.0 meV at 4 K in the $hk0$ zone on PONTA and in the hhl zone on TOPAN, respectively. (e),(f),(g) and (h) depict the calculated patterns of squared form factors of hexamer and heptamer, corresponding to the experimental data (a),(b),(c) and (d), respectively. The schematic pictures of these spin-molecule models are illustrated in (i) and (j). The spins dynamically fluctuate in arbitrary directions with the relative spin correlation shown in (i) and (j).

Fig. 2(j). The square of the form factor of the heptamer is also represented by Eq. (1), where N is replaced by 7, and $\langle\ \rangle$ means the average of the 32 types of spin correlations over the eight $\langle 111 \rangle$ directions and the four types ($8 \times 4 = 32$). Using the Watson-Freeman form factor again, we obtain the patterns of Figs. 2(g) and 2(h), which are both consistent with those of Figs. 2(c) and 2(d).

Thus, the first and second resonance levels in the magnetically ordered phase are identified to be the antiferromagnetic hexamer and heptamer. However, both of the spatial correlations of hexamer and heptamer have been emblematic of the paramagnetic phases of different systems with geometric frustration so far [3,10]. This fact suggests the following two points. First, a geometrically frustrated magnet essentially implies several magnetic modes. If a geometrically frustrated magnet transforms to a magnetically ordered phase, the first mode in the ordered phase will be the same as in a paramagnetic phase, i.e., the hexamer. The candidates for the high-order modes can appear in the paramagnetic phase similarly to other types of frustrated magnets, e.g., like the heptamer. Second, the high symmetry of the lattice is *dynamically* restored in the magnetically ordered phase with lattice distortion probably by the spin-lattice coupling, often caused by the geometric frustration [22–24]. In addition, as shown in Figs. 2(i) and 2(j), all the solid lines connecting the vertices are parallel to the $\langle 110 \rangle$ directions of the t_{2g} orbitals, d_{xy}, d_{yz} and d_{zx}, occupied by the three $3d$ electrons in the Cr^{3+} ion. Therefore, although $MgCr_2O_4$ possesses no freedom of orbital and valence, we consider that both spin-lattice coupling and orbital hybridization induce the local itinerancy of $3d$ electrons (charge freedom) within the molecules as the mechanism of spin-molecule states. This situation is similar to the quantum resonance in benzene. In fact, benzene is represented by the Kekule structure, in which every vertex possesses three branches (chemical bonds), but the molecular orbital hybridization with nonlocalized electrons stabilizes the resonance structure of the

real benzene, as described by a circle in a hexagon in the chemical structure [25].

The present spin-molecule states in the antiferromagnetic phase are experimentally characterized by the intermolecular independence and the discreteness of energy. The two features coincide with the concept of elementary excitation (quasiparticle) in the Landau's Fermi liquid approximation. In the Landau theory, the *strongly correlated electrons* behave like independent particles with fundamental energy quanta. Therefore, expanding the approximation to the spin system, we propose that the *highly frustrated spins* also act as quasiparticles (geometric quanta or geometrons). With this point of view, the spin correlations in paramagnetic phases are interpreted as the paramagnetic scattering of the lowest geometron mode. The modes of geometrons could be classified by the geometric or topologic parameters of spin molecules, such as the numbers of vertices, sides, or holes, as good quantum numbers.

In summary, the present experiments identified the spatial correlations of the two levels to be hexamers and heptamers in a magnetically ordered phase of the geometrically frustrated magnet $MgCr_2O_4$. We speculate that dynamical molecular spin states are induced by the coupling among electronic freedoms and lattice, which were not taken into account in the initial concept proposed by Wannier and Anderson [1,2]. Furthermore, phenomenologically, these spin molecules may be described by the geometron picture. Therefore in order to prove such conjecture, it is highly required to study systematically both spin excitations and lattice dynamics in the antiferromagnetic phase over a wide energy range for many geometrically frustrated magnets.

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