Spin-Singlet Ground State in the Two-Dimensional Frustrated Triangular Lattice: $YbAl_3C_3$

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We present the highly frustrated phenomena observed in $YbAl_3C_3$ with a spin gap. The inelastic neutron spectra of low-lying magnetic excitations at low temperatures are quite similar to those of $SrCu_2(BO_3)_2$ and $(CuCl)LaNb_2O_7$ that exhibit a dimer ground state in a two-dimensional quantum spin system. The structure of the first excited triplet state is directly clarified by inelastic neutron scattering experiments with a higher energy resolution. Furthermore, it becomes clear that the characteristic magnetic excitations remain within a high-temperature region. The result of the specific heat measurement also shows an anomaly associated with the formation of dimerized Yb ions. We conclude that a long-range magnetic order is suppressed by a large geometrical spin frustration, resulting in the stabilization of the dimer ground state.

KEYWORDS: frustrated triangular lattice, spin-singlet ground state, inelastic neutron scattering

A geometrical frustration has been investigated in the d-electron system over the past 50 years, and numerous frustrated compounds have been found in transition metal oxides, sulfides, and chlorides. On the other hand, recently, a study of the geometrical frustration effects in the f-electron system was carried out on several compounds. For example, in the pyrochlore oxide $Dy_2Ti_2O_7$, the frustration is considered to play an important role in the realization of a spin ice state.[1)] The weak magnetic interaction, which is estimated to be of the order of 1 K, is a characteristic of this compound. In rare-earth intermetallic compounds, the RB_4 series exhibits the phenomena related to the frustration. TbB_4 shows multistep metamagnetic transitions and a noncollinear magnetic structure.[2)] In DyB_4, the existence of the short-range correlation of the magnetic and quadrupolar components is suggested.[3,4)] All of them have the three-dimensional crystal structure.

For a two-dimensional quantum spin system with the geometrical frustration, there are some interesting reports of the dimer ground state that is realized in $SrCu_2(BO_3)_2$ with the Shastry-Sutherland lattice[5,6)] and square lattice compound $(CuCl)LaNb_2O_7$.[7,8)] These materials exhibit spin-gap behavior in magnetization, specific heat, and inelastic neutron scattering (INS) measurements.

Another important compound is Yb_4As_3. This compound has no magnetic ordering and a large paramagnetic Curie temperature $\theta_p \simeq -60$ K and is thereby classified into frustrated materials. INS experiments revealed that the dispersion relation was interpreted as a one-dimensional quantum spin system.[9)]

$YbAl_3C_3$ has a hexagonal unit cell with $c/a \approx 5.04$, and each layer, which is composed of Yb, Al, or C, stacks along the c axis. Accordingly, the network of Yb atoms can be regarded as a two-dimensional triangular lattice. We previously discussed the possibility of antiferroquadrupolar (AFQ) ordering at 80 K and pointed out the absence of the long-range magnetic order down to 2 K although this compound has a large θ_p of -94 K.[10)] The effective paramagnetic moment agrees well with the expected value for the Yb^{3+} ion. Furthermore, it has recently been confirmed by μSR experiments that there is no magnetic ordering down to 20 mK.[11)] Therefore, we consider that $YbAl_3C_3$ is a new system with a strong geometrical magnetic frustration.

Recently, A. Ochiai *et al.* claimed that the anomaly at 80 K is caused by a simple structural phase transition.[12)] However, the structural phase transition is extremely small, and the lattice parameters do not change within the accuracy of synchrotron X-ray diffraction measurements.[13)] Atoms are only slightly displaced. The intensities of the superlattice reflections in this experiment are of the same order as that of UPd_3, which shows an AFQ ordering accompanied by the structural phase transition.[14)] Moreover, we found that the transition temperature depends on the applied magnetic fields.[10)] The same behavior was also observed by nuclear magnetic and quadrupolar resonance measurements.[15,16)] Accordingly, it is considered that $4f$ electrons participate in the transition at 80 K.

In the paper reported by Ochiai *et al.*, they suggested the existence of the spin-gap state in $YbAl_3C_3$ as a $S = 1/2$ Heisenberg antiferromagnet.[12)] It seems that the results of the specific heat and magnetization measurements can be basically explained by the isolated dimer model. In this paper, we present the direct evidence for

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the singlet-triplet excitations in $YbAl_3C_3$ and interesting magnetic excitations in a high-temperature region. On the basis of these experimental results, we discuss the development of the dimerization between a pair of Yb ions at low temperatures.

The method and recipe of sample preparations are essentially identical to those reported previously.[10] In the present experiments, we have succeeded in growing single crystalline samples with a hexagonal prism shape, whose size was approximately ϕ20 μm $\times$ 1 mm. The specific heat and electrical resistivity measurements were carried out using these single crystals by the conventional relaxation method and the standard AC four-probe method, respectively. INS experiments were performed on the triple-axis spectrometer TOPAN and ISSP-HER installed at the JRR-3M reactor. For TOPAN, the data were collected using a fixed final neutron energy, E_f, of 14.8 meV (k_f = 2.67 Å^{-1}) and a set of the horizontal collimation of open-60′-(Sample)-(PG)-60′-open, where a pyrolytic graphite (PG) filter was placed after the sample in order to eliminate higher-order contaminations. ISSP-HER, the cold-neutron spectrometer, is equipped with a vertically focused PG (002) monochromator and a horizontally focused PG (002) analyzer and is operated with a fixed final energy, E_f, of 5.0 meV (k_f = 1.555 Å^{-1}) or 2.4 meV (k_f = 1.082 Å^{-1}). The collimations after the monochromator were open-(Sample)-radial collimator-open.

Figure 1(a) shows the inelastic neutron spectra of $YbAl_3C_3$ at 8 K, 60K, and 100 K and of $LuAl_3C_3$ at 8 K observed at q = 2.7 Å^{-1}. Well-defined excitations are observed around 14, 20, 33, and 43 meV. The peak around 33 meV is clearly attributed to magnetic excitation since no peak is found in the same energy region in the $LuAl_3C_3$ spectrum that shows only phonon contributions. On the other hand, phonon peaks appear around 14 and 43 meV in $LuAl_3C_3$. Accordingly, it is thought that the peak around 14 meV of $YbAl_3C_3$ is due to the phonon scattering. However, the peak around 43 meV includes a component of a magnetic excitation because the peak intensity decreases with increasing temperature. At this stage, we think that the peak around 20 meV is a magnetic excitation because of the absence of phonon structures although this peak is almost independent of temperature. As a result, the three peaks around 20, 33, and 43 meV that are indicated with arrows are considered to originate from magnetic excitations. This result implies that the J-multiplet of the Yb^{3+} ion is split into four Kramers doublets by the hexagonal crystalline electric field (CEF) effects. In addition, the intensity of magnetic excitation increases usually with decreasing temperature. However, the peak intensity around 33 meV exhibits an unusual temperature dependence between 100 K and 60 K. As a possibility, we point out that the wave functions of the CEF state begin to change with interactions among the Yb ions below the phase transition at 80 K. The large difference in the peak shape between 60 K and 8 K originates from a drastic change in the ground state at low temperatures, as will be discussed in the next paragraph.

Figure 1(b) shows the inelastic neutron spectra of $YbAl_3C_3$ in the energy transfer region below 4 meV at various temperatures. The magnetic excitations are observed around 1.5 and 2.9 meV. The intensities of these two peaks reduce rapidly with increasing temperature and then the shapes gradually change into one broad peak. Finally, the peak seems to flatten toward approximately 80 K where a deviation of the magnetic susceptibility from the Curie-Weiss law is seen; this corresponds to the phase transition at 80 K. We think that these low-energy peaks correspond to some magnetic excitations associated with the gaps that are generated by the magnetic interaction between neighboring CEF ground doublets. Such a split of CEF ground doublet is unusual since no magnetic long-range order can be observed down to 20 mK.[11] Besides, the dispersion is expected to be almost flat since the excitations are clearly observed in spite of performing the experiments on powder samples.

We performed a detailed observation in order to examine the structure of these excited states. Figure 2 shows the spectra measured using E_f = 2.4 meV with a high resolution of 0.06 meV at T = 0.7 K. As a result, it became clear that the first excited state consists of three excitations and the second excited state is composed of

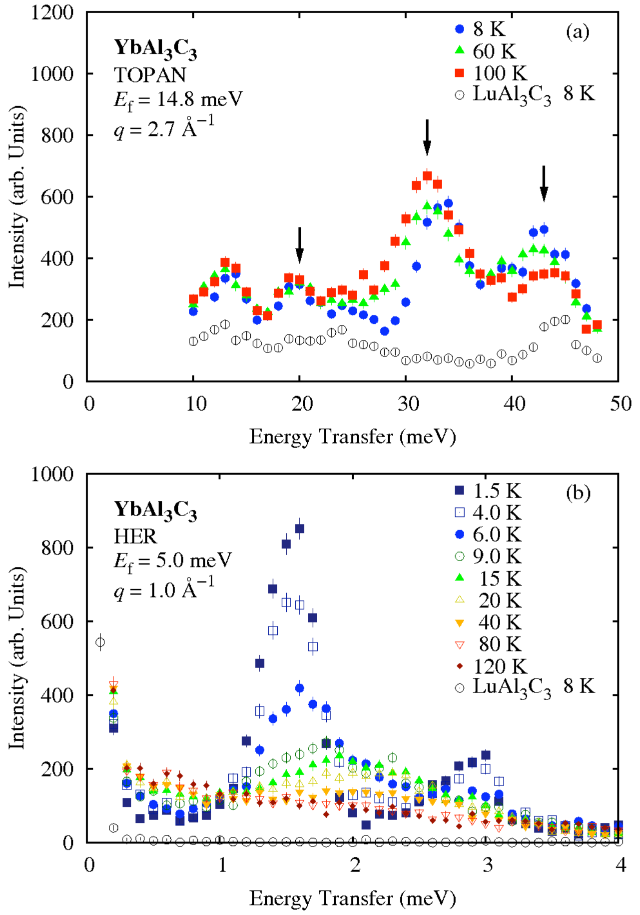

Fig. 1. (a) Inelastic neutron spectra of $YbAl_3C_3$ at 8 K (closed blue circles), 60 K (closed green triangles), and 100 K (closed red squares) and of $LuAl_3C_3$ at 8 K (open black circles). (b) Temperature dependence of the low-energy inelastic neutron spectra observed for $YbAl_3C_3$ at various temperatures and for $LuAl_3C_3$ at 8 K.

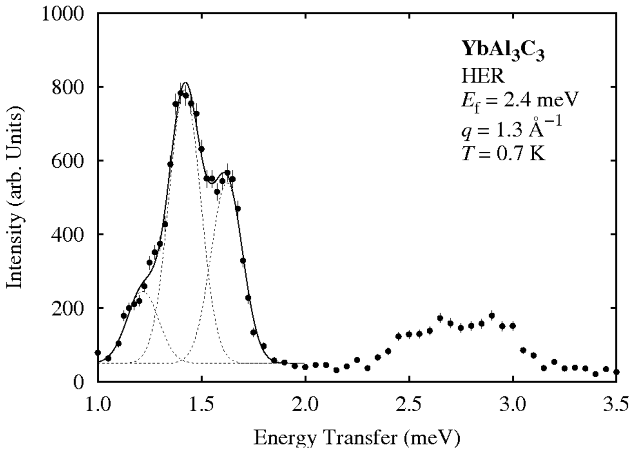

Fig. 2. Detailed inelastic neutron spectra of $YbAl_3C_3$ at 0.7 K with $E_{\mathrm{f}} = 2.4$ meV. The full curve represents the least-squares fit where the peaks are approximated by three Gaussian curves (see text).

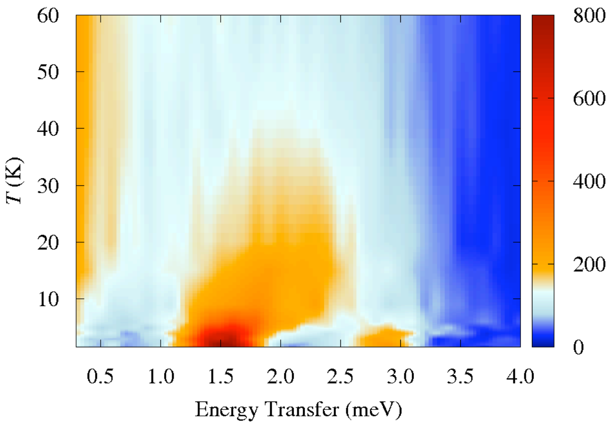

Fig. 3. Color contour map of the temperature dependence of low-lying excitations of $YbAl_3C_3$ that is obtained by replotting Fig. 1(b).

many excitations. The solid line shows the least-squares fit to the experimental data where the peaks are approximated by three Gaussian curves. The excitation energies are estimated to be 1.22, 1.42, and 1.62 meV using the same full widths at the half maximum of 0.18 meV. In single crystalline $SrCu_2(BO_3)_2$, the three resolved branches of the triplet excitation, which are attributed to the Dzyaloshinski-Moriya interaction, were observed by high-resolution INS experiments.[17] The crystal symmetry of $YbAl_3C_3$ lowers below the phase transition at 80 K; this will satisfy the condition of the Dzyaloshinski-Moriya interaction. When we consider the analogy between the results of the INS measurements for these two compounds, the first and the second excitations are expected to be the single-triplet excitations and two-triplet excitations, respectively. Moreover, the energy gaps, $\Delta_1 \simeq 1.5$ and $\Delta_2 \simeq 2.9$ meV, satisfy the relation $\Delta_2 \approx 2\Delta_1$.

The existence of the triplet state was established at

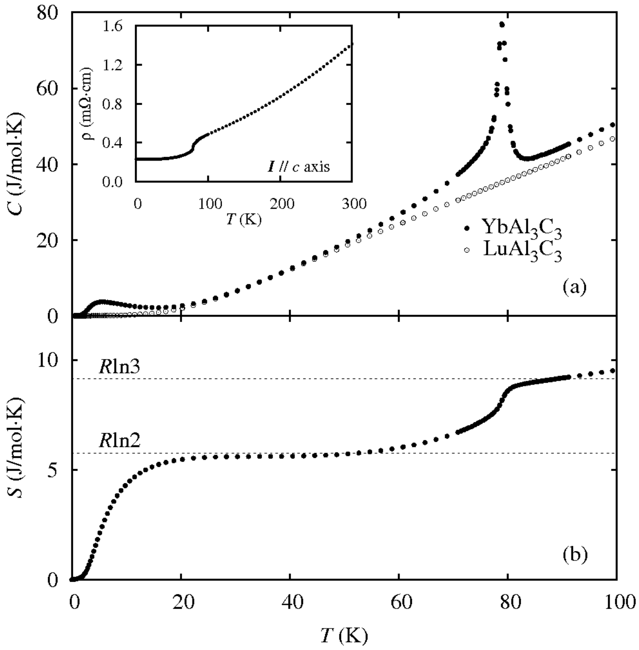

Fig. 4. (a) Temperature dependence of the specific heat of $YbAl_3C_3$ (closed circles) and $LuAl_3C_3$ (open circles). The inset shows the the electrical resistivity as a function of temperature for the current along the c axis. (b) Temperature dependence of the magnetic entropy in $YbAl_3C_3$.

low temperatures, as described above. However, the intensities of triplet excitations exhibited an unusual temperature dependence. Figure 3 shows the color contour map that is obtained by replotting Fig. 1(b) for the purpose of understanding the temperature dependence of low-lying excitations. In the case of $SrCu_2(BO_3)_2$ and $(CuCl)LaNb_2O_7$, the intensities of single-triplet excitations and two-triplet excitations decrease with increasing temperature and then disappear around the temperature where the magnetic susceptibility as a function of temperature indicates the maximum. The temperature dependence of magnetic susceptibility of $YbAl_3C_3$ is maximum around $T_{max} = 9$ K. The characteristic structure associated with one or two triplet states, especially the excitations around 2.9 meV, seems to vanish toward 9 K. In other words, the dimerization between a pair of Yb ions develops below T_{max}. However, the obvious magnetic excitations still remain above T_{max}, and the center of the peak shifts gradually toward a higher energy. The origin of these magnetic excitations in a high-temperature region has not been clarified as yet. This phenomenon has not been observed in the d-electron quantum spin system. Therefore, it is speculated that these excitations are concerned with the frustration of competing magnetic interactions on a triangular lattice.

Figure 4(a) shows the temperature dependence of the specific heat of $YbAl_3C_3$ using many small single crystals down to 0.4 K. We carried out the specific heat measurements several times using different batches and confirmed the reproducibility carefully. An obvious anomaly was detected at 80 K, and a Schottky anomaly was found at around 5 K. We obtained the magnetic contribution to

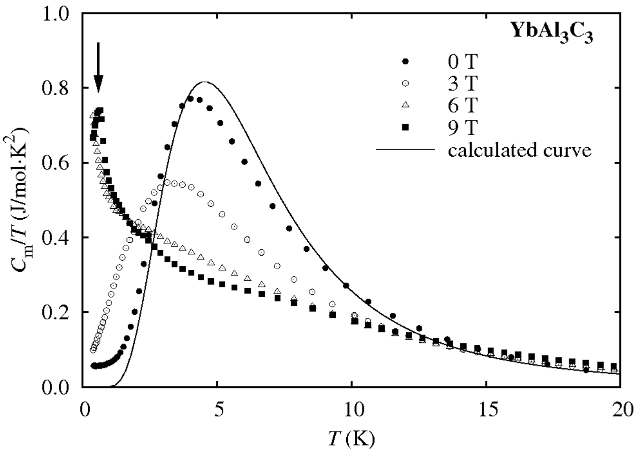

Fig. 5. C_m/T versus T of $YbAl_3C_3$ measured at various magnetic fields. Solid curve shows the calculated curve based on the singlet-triplet model normalized to 1 mol of Yb ions (see text).

the specific heat by subtracting the phonon portion that was assumed to be the same as that of $LuAl_3C_3$. Here, it must be noted that the released magnetic entropy for the Schottky anomaly was estimated to be exactly $R \ln 2$, as shown in Fig. 4(b). This result is consistent with the dimer model. However, the reason for the value of $R \ln 3$ at around 80 K has not been clarified as yet. We consider that the released entropy at around 80 K includes a contribution from the f-electron system since the change in the wave functions of the CEF state will occur before and after the phase transition, as mentioned in the discussion on Fig. 1(a).

The inset of Fig. 4(a) shows electrical resistivity as a function of temperature for the current along the c axis. The anomaly associated with the phase transition at 80 K is clearly observed. Comparison with the previous report[12] indicates that the anisotropy of the resistivity is not large for the directions of the current. It is important to note that no Kondo effect was detected in the electrical resistivity; therefore, the absence of magnetic ordering is not due to the formation of the Kondo singlet ground state. Furthermore, no remarkable features were found in the temperature region of the development of the dimer, suggesting that the $4f$ electrons are not relevant to conductivity.

The magnetic specific heat divided by the temperature around the Schottky anomaly measured under zero magnetic field is plotted as a function of temperature by using filled circles in Fig. 5. The calculated curve, which is based on a singlet-triplet model using the gaps determined from Fig. 2, is in good agreement with the experimental result. When the magnetic field was applied, the maximum of the Schottky anomaly shifted toward lower temperatures rapidly and then the gap collapsed above 6 T. Furthermore, a cusp indicated with the arrow was found at 0.7 K under the magnetic field of 9 T. There is the possibility that this cusp exhibits a phase transition similar to that observed in $(CuCl)LaNb_2O_7$[8] and $TlCuCl_3$[18] under magnetic fields.

Let us discuss the reason for the dimerization of Yb^{3+} ions at low temperatures. The primary factor is considered to be the two-dimensionality of the crystal structure of $YbAl_3C_3$ and the triangular lattice formed by the Yb ions. Therefore, a geometrical frustration is basically included in $YbAl_3C_3$. The rare-earth intermetallic compounds having the Kramers doublet ground state are usually ordered magnetically in order to release the magnetic entropy of the ground state. However, in this case, a long-range magnetic order is suppressed by the frustration although θ_p indicates a large antiferromagnetic interaction. A secondary factor is the slight displacement of atoms at 80 K. The triangular lattice is almost maintained even below 80 K. However, the magnetic interaction among the Yb ions is no longer exactly identical. As a result, it is thought that the system tends to the dimerization at low temperatures in order to lift the degeneracy of the ground state by using the small difference in the magnetic interactions. From this, we consider that the dimerization is not very strong; therefore, the magnetic entropy of $R \ln 2$ is easily released.

Further, we would like to state that the discussion based on the quantum spin model is considered to be applicable to $YbAl_3C_3$ as well as Yb_4As_3 since the dimerization in itself is the result of quantum effects.

To summarize, we have demonstrated the direct observation of the singlet-triplet excitations in the two-dimensional frustrated compound $YbAl_3C_3$. In this material, the frustration plays an important role in forming the dimer ground state. In order to determine the structure of the dimerized Yb ions, further measurements such as neutron diffraction experiments under magnetic fields using a single crystal are required.

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