Novel Ordering of an $S = 1/2$ Quasi-1d Ising-Like Antiferromagnet in Magnetic Field

S. Kimura,[1] T. Takeuchi,[2] K. Okunishi,[3] M. Hagiwara,[1] Z. He,[4] K Kindo,[4] T. Taniyama,[5] and M. Itoh[5]
[1]*KYOKUGEN, Osaka University, Machikaneyama 1-3, Toyanaka 560-8531, Japan*
[2]*Low temperature center, Osaka University, Machikaneyama 1-1, Toyanaka 560-0043, Japan*
[3]*Department of Physics, Niigata University, Niigata 950-2181, Japan*
[4]*Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8531, Japan*
[5]*Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori Yokohama 226-8503, Japan*
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High-field specific heat measurements on $BaCo_2V_2O_8$, which is a good realization of an $S = 1/2$ quasi-one-dimensional (1D) Ising-like antifferomagnet, have been performed in magnetic fields up to 12 T along the chain and at temperature down to 200 mK. We have found a new magnetic ordered state in the field-induced phase above $H_c \simeq 3.9$ T. We suggest that a novel type of the incommensurate order, which is caused by the quantum effect inherent in the $S = 1/2$ quasi-1D Ising-like antiferromagnet, appears in the field-induced phase.

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The $S = 1/2$ one-dimensional (1D) antiferromagnetic XXZ model is a simple spin system but exhibits very rich and exotic properties originating from quantum fluctuation inherent in the model. It is one of a few examples of many-body quantum systems, being exactly solvable by the Bethe ansatz, and has been the object of numerous theoretical studies. An important feature of this model is a quantum critical nature of the ground state, characterized by power law decay of the correlation function in its gapless spin liquid phase [1,2]. The quantum critical nature is a manifestation of the Tomonaga-Luttinger (TL) liquid state, which realizes in this gapless phase. A magnetic field for the longitudinal z-direction can play a key role in controlling this aspect [2,3]. The model is given by the Hamiltonian

$$\mathcal{H} = J\sum_i \{S_{i,z}S_{i+1,z} + \epsilon(S_{i,x}S_{i+1,x} + S_{i,y}S_{i+1,y})\} - g\mu_B \sum_i S_{i,z}H \quad (1)$$

where, $J > 0$ is the antiferromagnetic exchange interaction, and $\epsilon \geq 0$ is an anisotropic parameter. The ϵ-h phase diagram for the ground state of the model, given by the Bethe ansatz calculations [3,4], is shown in Fig. 1. Here, $h = g\mu_B H/J$ is the normalized field. Peculiar quantum critical behaviors in the fields were theoretically demonstrated in the spin liquid phase. An incommensurate correlation for the longitudinal spin component develops, in addition to a transverse staggered one [2]. Asymptotic forms of the transverse and longitudinal correlation functions are expressed, respectively, as follows:

$$\langle S_0^x S_r^x \rangle \simeq (-1)^r r^{-\eta_x} \quad (2)$$

and

$$\langle S_0^z S_r^z \rangle - m^2 \simeq \cos(2k_F r) r^{-\eta_z} \quad (3)$$

where m is a magnetization per spin, η_x and η_z are the TL exponents for the x and z spin component, respectively, which satisfy a relation $\eta_x\eta_z = 1$ and $k_F = \pi(1/2 - m)$.

In this Letter, we discuss the quasi-1D $S = 1/2$ Ising-like antiferromagnet with $\epsilon < 1$ in the longitudinal fields at very low temperature. Inevitable three-dimensional (3D) interactions in real quasi-1D materials make the quantum critical state unstable, and can lead to a long range order at a finite temperature. As a result, the magnetic ordering with exotic properties, reflecting the peculiar quantum critical nature of the 1D XXZ model, is expected to appear in the quasi-1D Ising-like antiferromagnet. Figure 1 shows that a quantum phase transition from the Néel ordered phase to the quantum critical spin liquid one occurs at a critical field H_c in the Ising-like system [2,3]. An important point for the Ising-like XXZ case is that the incommensurate correlation is enhanced above the critical field H_c, in contrast to

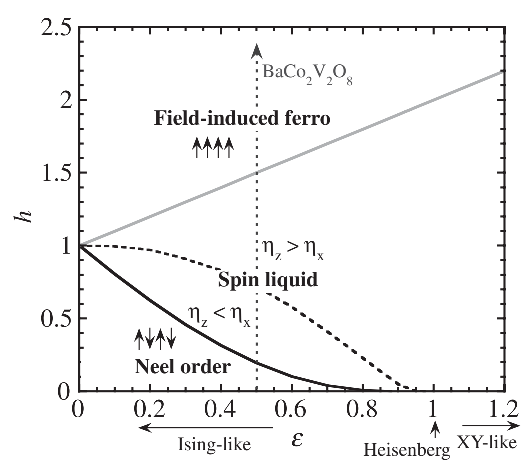

FIG. 1. ϵ-h phase diagram for 1D $S = 1/2$ antiferromagnetic XXZ model. Black and gray lines show the transition field and the saturation field, respectively. Dashed line shows the field at which the crossover of the TL components occurs.

the usual isotropic Heisenberg model, for which the staggered correlation of the xy spin components is always dominant in a magnetic field. Then the interchain coupling brings a quite interesting situation in the gapless phase above H_c, as will be argued later. We will report the first observation of the magnetic ordering in the field-induced phase of the $S = 1/2$ quasi-1D Ising-like antiferromagnet above H_c by specific heat measurements on $BaCo_2V_2O_8$.

In $BaCo_2V_2O_8$, a magnetic Co^{2+} ion is surrounded by six oxygen atoms, and the edge shared CoO_6 octahedra form a screw chain along the c-axis [5]. At zero field, $BaCo_2V_2O_8$ undergoes a long range ordering at 5.4 K [6–8]. When the external field is applied for the c-axis, which is the easy axis of $BaCo_2V_2O_8$, a field-induced transition occurs at $H_c \simeq 3.9$ T, as shown in Fig. 2 [6,7,9,10]. In contrast to the spinflop transition of classical antiferromagnets with easy-axis anisotropy, which exhibits a linear increase of the magnetization above the transition field, the magnetization in $BaCo_2V_2O_8$ shows a nonlinear and steep increase above H_c. This behavior suggests strong quantum fluctuation in the field-induced phase. In fact, previous specific heat measurements showed that no magnetic ordering was observed down to 1.8 K in the field-induced phase for $H > H_c$ [6,7]. Therefore, the field-induced transition in the temperature region above 1.8 K causes a destruction of the long range magnetic order. [6,7]. In our recent study, we revealed that the above-mentioned quantum phase transition of the $S = 1/2$ 1D Ising-like antiferromagnet, which brings about the quantum critical nature in the field-induced phase, is responsible for the destruction of the magnetic order in $BaCo_2V_2O_8$ [9,10]. The magnetization curve is explained by the $S = 1/2$ 1D XXZ model with $\epsilon \simeq 0.5$, $g = 6.2$, and $J/k_B = 65$ K, as shown in Fig. 2. An advantage of $BaCo_2V_2O_8$ is its rather low critical field $H_c \simeq 3.9$ T that is easily accessible by commercial superconducting magnets. Thus, $BaCo_2V_2O_8$ is very suitable material for studies of the field-induced phase in the $S = 1/2$ quasi-1D Ising-like antiferromagnet. In this study, with further decreasing temperature by using a dilution refrigerator, we find a new long range ordered phase above H_c. The transition between the Néel ordered phase to the field-induced ordered one is revealed to be of first order. From the theoretical considerations based on the Bethe ansatz calculations, we propose that a novel type of the incommensurate order is realized in the field-induced phase.

The specific heat of $BaCo_2V_2O_8$ for $H \parallel c$ was measured by means of a quasiadiabatic heat pulse method in high magnetic field up to 12 T and at temperature down to 200 mK. We use a dilution refrigerator and a superconducting magnet. Magneto-caloric effect was also measured. Single crystals of $BaCo_2V_2O_8$, grown by a spontaneous nucleation method [8], were used for the measurements.

Figure 3 shows the temperature dependence of the heat capacity observed in $BaCo_2V_2O_8$ for $H \parallel c$. In the field region above H_c, a λ-peak, which corresponds to the long range magnetic order, is observed at temperature below 1.8 K. As the field is increased, the peak position shifts toward lower temperature. The λ-peak diminishes with increasing the field and disappear in the field region above 10 T. Slight upturn of the specific heat is seen in the low temperature region, presumably owing to the contribution from the nuclear magnetism. The observed ordering temperatures are plotted together with the data obtained from the previous measurements by He *et al.* [6,7] and the transition fields determined by the magnetization and magetocarolic effect measurements in Fig. 4. The inset of Fig. 4 shows the field dependence of magnetocarolic effect. Sharp peaks at $H_c \simeq 3.9$ T, accompanied by a small hysteresis, exhibit a phase boundary of weak first order, as

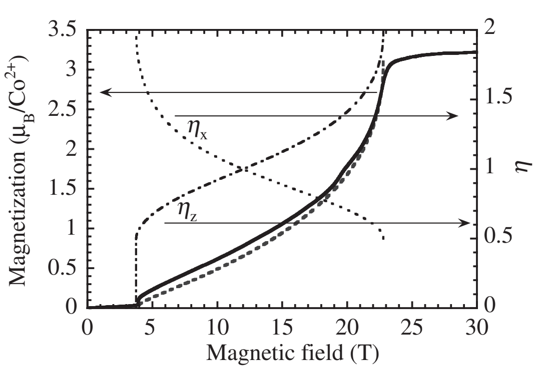

FIG. 2. Magnetization curve of $BaCo_2V_2O_8$ and the calculated TL exponents. Solid and gray dashed lines are the experimental and theoretical magnetization curves, respectively. The Van Vleck paramagnetic contribution is subtracted from the experimental magnetization curve. Dotted and dot-dashed lines shows the TL exponents η_x and η_z, respectively.

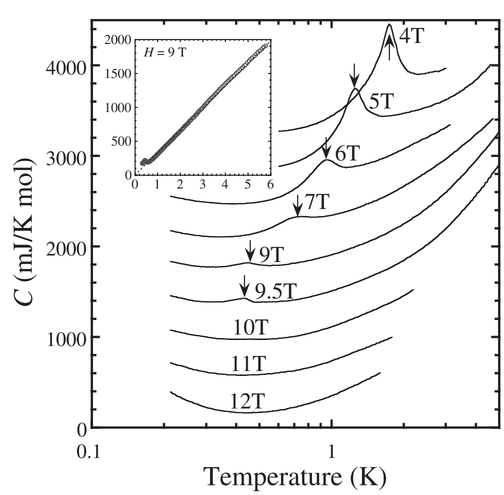

FIG. 3. Temperature dependence of the specific heat of $BaCo_2V_2O_8$ for $H \parallel c$. Each specific heat shifts up by 400 mJ/K mol with decreasing field from 12 T. Inset shows an extended figure of the specific heat observed at 9 T. Open circles are the experimental data and dashed line is a guide for the eye.

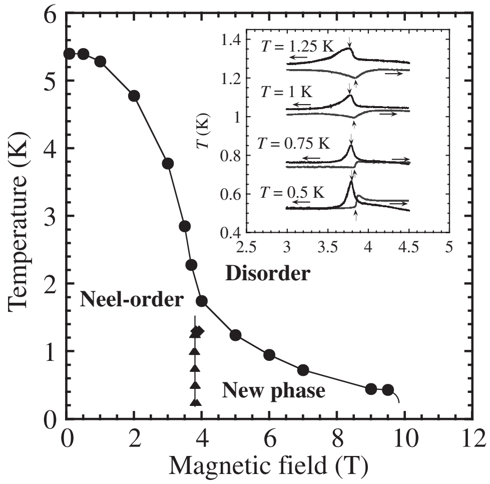

FIG. 4. Phase diagram of $BaCo_2V_2O_8$ for $H \parallel c$. Closed circles show the transition temperatures determined from the heat capacity measurements. Diamonds and triangles show the transition fields determined from the magnetization curves and magnetocarolic effects, respectively. Solid curves are guides for the eye. Inset shows the results of the magnetocarolic effect measurements. Gray and black curves show the experimental data, observed in the field-ascending and descending processes, respectively.

plotted by triangles in Fig. 4. Thus, our measurements reveal the appearance of a new ordered state in the field-induced phase above $H_c \simeq 3.9$ T at temperature below 1.8 K. The peaks, found in the magneto-caloric effects at H_c, show that the transition between the Néel ordered phase to the field-induced ordered one is accompanied by latent heat. The phase boundary between the Néel order and the new phase has almost no field dependence, and is of first order. Such a phase boundary is hardly determined by the specific heat measurements. Thus, we adopted the magneto-caloric-effect measurement. The concave peak, which corresponds to an endothermic behavior of the sample, in the field-ascending process suggests larger entropy in the field-induced phase compared with the Néel ordered one.

As we mentioned before, a gapless spin liquid state realizes in the field region above the transition field H_c for ideal 1D $S = 1/2$ Ising-like antiferromagnets. The magnetic excitation in the spin liquid state is characterized by k-linear dispersion with soft mode at incommensurate wave vectors [2]. Our previous ESR measurements on $BaCo_2V_2O_8$ at 1.3 K suggested the development of such incommensurate soft modes for $H > H_c$ [10]. A T-linear dependence of the specific heat above the ordering temperature, indicative of the gapless k-linear dispersion [11], further supports a realization of the gapless spin liquid state; see the inset of Fig. 3. For the Heisenberg or XY system with $\epsilon \geq 1$, the transverse staggered correlation is always dominant compared with the longitudinal one in the spin liquid phase up to the saturation field as shown in Fig. 1 [3]. Therefore, usual Néel type ordering of the transverse spin components should take place in the quasi-1D XY or Heisenberg antiferromagnet. The quantum critical behavior of the Ising-like system, however, is quite different from that of the system with $\epsilon \geq 1$. Dotted and dot-dashed lines in Fig. 2 show the field dependences of the TL exponents η_x and η_z for the $S = 1/2$ 1D XXZ model, respectively, calculated by the Bethe ansatz integral equation [3] with $\epsilon = 0.46$, $g = 6.2$ and $J/k_B = 62.5$ K. These parameters were estimated from the analysis of the magnetization curve [9]. It should be mentioned that a small ferromagnetic next-nearest neighbor (NNN) intrachain interaction in $BaCo_2V_2O_8$ was suggested from our ESR measurements [10]. However, the NNN interaction is neglected in this discussion because it is estimated to be less than 10% of the nearest neighbor one. In contrast to the Heisenberg or XY system, $\eta_z < \eta_x$, which indicates a dominance of the longitudinal incommensurate correlation compared with the transverse one, is satisfied for the Ising-like system in a certain field region above H_c. When the 3D interaction is relevant, the dominant longitudinal correlation in the chain is expected to develop to the long range order for the quasi-1D material. Thus, we propose that the long range ordered phase with an incommensurate spin structure appears in $BaCo_2V_2O_8$ above H_c. In this structure, the spins align to be colinear along the c-axis with modulation of those amplitude, characterized by the incommensurate wave number $k = 2k_F$. Actually, the recent theoretical study demonstrated that such an incommensurate order, which results from the dominance of the η_z, can be stabilized by the interchain molecular fields for the $S = 1/2$ bond-alternating chain system with frustration [12]. The concave curve of the phase boundary between the ordered phase in the field-induced region and the disordered one in $BaCo_2V_2O_8$ is qualitatively different from convex phase boundaries found in the Heisenberg spin gap systems, such as $TlCuCl_3$ [13], for which the ordering of transverse spin components appears. We consider that this reflects the difference of the spin structures in the ordered phase. The appearance of the incommensurate order in the longitudinal field was discussed for the first time in the $S = 1$ quantum 1D chain with large single-ion type easy-axis anisotropy [14]. To our knowledge, however, the incommensurate order in such a system has not been confirmed experimentally yet.

In the ordered phase above H_c, the incommensurate soft mode will turn into the gapless Goldstone mode as a consequence of the breaking of a quasicontinuous translation symmetry, whereas the magnetic excitation in the Néel ordered phase of the Ising-like system has a finite gap [15]. Thermal excitation is activated in presence of the gapless mode, giving rise to the larger entropy for the field-induced phase, as suggested by the magneto-caloric effect. With further increasing of the field, a crossover of the TL exponents between η_x and η_z occurs, and then the transverse correlation becomes dominant in the 1D chain, as shown in Fig. 2. The disappearance of the long range order above 10 T may be attributed to this crossover. Around the crossover field, the long range order should be suppressed, as the order of both the longitudinal and transverse spin components usually cannot coexist. Competition between these two kinds of order, which becomes significant around the crossover field because of the equivalence between the η_x and η_z, disturbs the system in taking a unique stable spin structure. In the higher field region above 12 T, we also expect an appearance of another phase, characterized by staggered order with respect to the xy spin components, owing to a development of the dominant transverse correlation.

Recent quantum Monte Carlo simulation showed that the incommensurate long range order can be stabilized only by the interchain exchange interaction for the $S = 1/2$ quasi-1D XXZ model [16], and a recent mean field analysis suggested that the interchain interaction in $BaCo_2V_2O_8$ is order of $1/1000$ of the intrachain one [17]. It should be mentioned that this incommensurate order is different from the spin density wave state of conducting linear chain systems, which is arisen by the nesting of Fermi surface. The incommensurate order appears also in the classical localized spin systems [18]. However, such an order in classical magnets usually occurs only for the system with competing interaction . In contrast to this, the incommensurate order in the quasi-1D Ising-like XXZ case is entirely due to the quantum fluctuation inherent in the system. It is theoretically known that the $S = 1/2$ 1D XXZ model can be represented by pseudofermion [19,20]. The field-induced quantum phase transition in the $S = 1/2$ 1D Ising-like antiferromagnet is described as that from the charge ordered phase with alternative alignments of the hole and pseudofermion to the TL liquid one with an incommensurate charge density wave (CDW) correlation of the pseudofermion. The incommensurate order of the longitudinal spin component in the $S = 1/2$ 1D XXZ model is a spin version of the CDW order for the pseudofermion. Such a CDW order, corresponding to the incommensurate order for the spin chain, is likely assisted by the spin-lattice coupling [21]. As the orbital degeneracy of Co^{2+} is not lifted by the octahedral cubic ligand field [22,23], relatively strong spin-lattice coupling is anticipated in $BaCo_2V_2O_8$. For more detailed studies of the ordered state in $BaCo_2V_2O_8$ above H_c, direct observations of the spin and lattice structures by neutron scattering measurements are desired.

In conclusion, we have observed the magnetic ordering in the field-induced phase of $S = 1/2$ quasi-1D Ising-like antiferromagnet above H_c for the first time by specific heat measurements on $BaCo_2V_2O_8$. We propose an appearance of an incommensurate order, reflecting the quantum nature of the $S = 1/2$ quasi-1D XXZ system.

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