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Observation of Bose–Einstein Condensation of Triplons in Quasi 1D Spin-Gap System $Pb_2V_3O_9$

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We observed a field-induced magnetic ordering in the quasi one-dimensional antiferromagnetic alternating chain system $Pb_2V_3O_9$ for the first time. The characteristic temperature dependence of the magnetic susceptibility below T_N and the power law behavior of phase boundary between paramagnetic and ordered phases in the $Pb_2V_3O_9$ system can be comprehended in terms of Bose–Einstein condensation of triplons, as in the case of $TlCuCl_3$ [Phys. Rev. Lett. **84** (2000) 5868]. Our results indicate that BEC of triplons can be observed in the present strongly-coupled-dimer system, while $TlCuCl_3$ is a weak inter dimer coupling system.

KEYWORDS: Bose–Einstein condensation of triplons, field-induced magnetic ordering, alternating chain, spin-gap, $Pb_2V_3O_9$
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1. Introduction

The Bose–Einstein condensation (BEC) is one of the most attractive topics in modern physics. The BEC of dilute alkali atoms has been achieved according to the development of the laser cooling technique.[1,2] For solid state physics, it has been indicated that field-induced triplets (*triplons*)[3] in a dimer-gap system behave as quasiparticles and can exhibit the BEC.[4] These triplons can be regarded as hard core bosons. When the off-diagonal mixing between adjacent dimer spins exists, the triplons can move and behave as a bose gas in the system. As temperature decreases, the triplons undergo the BEC at a transition temperature T_N. The triplon BEC is experimentally observed as the antiferromagnetic long range ordering of the transverse spin components, perpendicular to an applied magnetic field. Some characteristic behaviors around T_N are predicted in the triplon BEC theory. One of the features is the minimum of magnetization at T_N. The magnetization is in proportion to the number of triplons, which are thermally excited and condensed below T_N. The thermally excited triplons decrease as decreasing temperature while the condensed ones increase below T_N. Thus the condensation of triplons gives the minimum of magnetization at T_N. Another feature is power law behavior of the phase boundary between the BEC and normal states with respect to temperature in the magnetic field phase diagram. The phase boundary can be expressed by the following power law:

$$(g/2)[H_c(T) - H_g] \propto T^{\phi}, \tag{1}$$

where H_g is the critical field at $T = 0\,\mathrm{K}$, and ϕ the critical exponent. Although this theory can explain the experimental data of field-induced magnetic ordering in $TlCuCl_3$ qualitatively, some disagreements between the theory and experimental data are found. One of the problems is the value of the critical exponent of the phase boundary. A Hartree–Fock approximation gives $\phi = 1.5$,[4] while the critical exponent is estimated experimentally to be $\phi = 2.2$ for $TlCuCl_3$.[4] The other is a discontinuous jump of the magnetization at T_N, predicted by a Hartree–Fock description, which has not been observed experimentally.

The BEC of triplons is expected to be observed in many isotropic spin-gap systems. Therefore, many spin-gap systems must be investigated from the aspect of the BEC and the critical exponent of the phase boundary should be decided experimentally. In this paper we present a possible perspective of the BEC of triplons in one of quasi one-dimensional (1D) systems, $Pb_2V_3O_9$.

In this compound, there are three kinds of vanadium ions in the unit cell. Two of them are the nonmagnetic V^{5+} ions, located in VO_4 tetrahedrons, and the rest one is V^{4+} ion with $S = 1/2$ in the VO_6 octahedron. Each VO_6 octahedron links in the corner sharing configuration.[5] As shown in Fig. 1, V^{4+} spins are located in two sites alternately and construct $S = 1/2$ alternating spin chain. The Hamiltonian for 1D alternating Heisenberg chain is given by

$$H = -\sum_{i=1}^{N/2}(J_1 S_{2i-1} \cdot S_{2i} + J_2 S_{2i} \cdot S_{2i+1}), \tag{2}$$

where N is the number of spins, J_1 the exchange integral of the nearest neighbor interaction, and J_2 that of the next nearest neighbor interaction. From the numerical results, the ground state of this model is of spin-singlet when $J_2 \neq 0$.[6,7] The temperature dependence of magnetic susceptibility χ of $Pb_2V_3O_9$ shows a peak around 20 K, and decreases markedly toward zero as temperature decreases, indicating spin-singlet ground state. The behavior can be well analyzed with $S = 1/2$ 1D antiferromagnetic alternating Heisenberg chain (1DAFAHC) model equation.[6,7]

2. Experiments

A polycrystalline sample of $Pb_2V_3O_9$ was prepared by the heat treatment of the mixing powders of PbO, V_2O_3 and V_2O_5 in the molar ratio of 8 : 1 : 5 in a sealed evacuated

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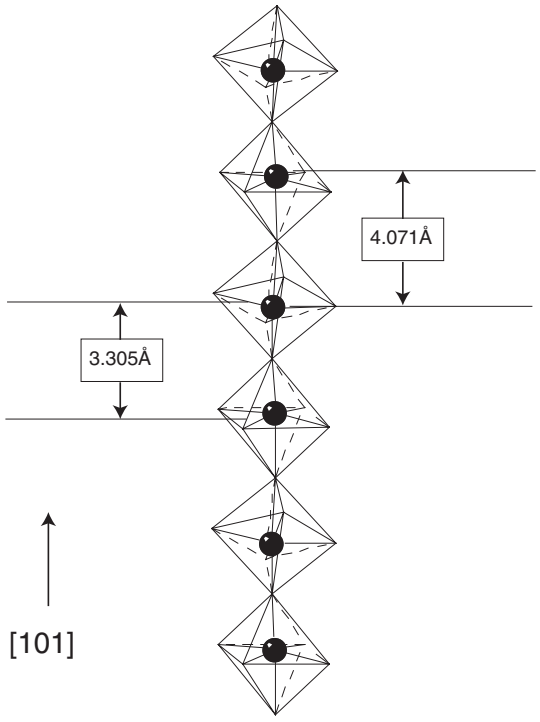

Fig. 1. Schematic V^{4+} chain in $Pb_2V_3O_9$. The chain is constructed with VO_6 octahedra linking in the coner sharing configuration along [101] direction. There are two kinds of V^{4+}–V^{4+} distance, forming $S = 1/2$ alternating chain.

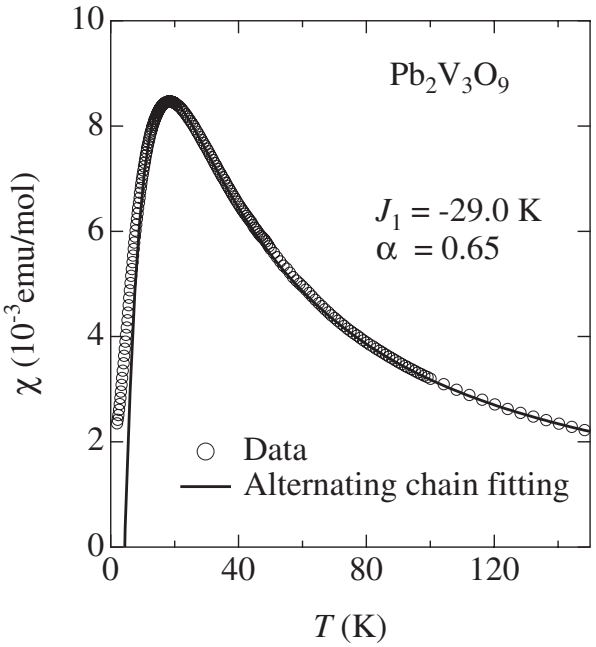

Fig. 2. Temperature dependence of the magnetic susceptibility of $Pb_2V_3O_9$. Open circles represent raw data, the solid line the fitting results using the alternating chain model with $J_1 = -29.0$ K and $\alpha = 0.65$.

silica tube up to 923 K for 2 days. The obtained sample was found to be in a single phase by powder X-ray diffraction measurement. The temperature dependence of the magnetic susceptibility was measured by the SQUID magnetometer under several magnetic fields up to 7 T. The high field magnetization was measured at 1.5 K in pulsed magnetic field up to 46 T with a pulse duration of 20 ms. The specific heat was measured by relaxation method under magnetic field up to 7 T with temperature down to 0.35 K.

3. Results and Discussion

Figure 2 shows the temperature dependence of χ in $Pb_2V_3O_9$ measured under 1 T. Above 100 K, χ follows the modified Curie–Weiss law, $\chi(T) = \chi_0 + C/(T - \theta)$, where χ_0 is a temperature-independent susceptibility, C the Curie constant and θ the Weiss temperature. The obtained parameters were found to be $\chi_0 = -6.7 \times 10^{-5}$ emu/mol, $C = 0.368$ emu/(K mol), which corresponding to $P_{\mathrm{eff}} = 1.71\,\mu_{\mathrm{B}}$ agreeing with $S = 1/2$, and $\theta = -12.3$ K. As temperature decreases, χ shows maximum around 20 K in agreement with 1D magnetic character. Below the temperature at which χ shows the maximum, χ decreases markedly. We fitted the data between 8 and 300 K using the 1DAFAHC model function with $S = 1/2$.[8,9] Our best-fitted values of parameters were $J_1/k_{\mathrm{B}} = -29.0$ K and $\alpha = 0.65$, where α is an alternation parameter defined as $\alpha = J_2/J_1$. The value of $\alpha = 0.65$ indicates that dimers are strongly couple each other in this system. These values are similar to those reported previously as $J_1/k_{\mathrm{B}} = -29.2$ K, $J_2/k_{\mathrm{B}} = -19.3$ K, $\alpha = 0.66$.[10] If we assume 1DAFAHC model without the other small interactions, the gap can be estimated as $\Delta_{\mathrm{cal}}/k_{\mathrm{B}} = 15$ K.[7] The extrapolation of the fitting line below 8 K deviates downward from the experimental data, because the used function can be available above $T = 0.25J_1/k_{\mathrm{B}}$.[8,9]

The fact that χ approaches zero with decreasing temperature indicates the spin-singlet ground state of this compound. In addition to this fact, the direct proof of the spin-singlet ground state was obtained by the magnetization measurement at 1.52 K using pulsed high-magnetic fields as shown in Fig. 3(a). With increasing magnetic field, the magnetization is first suppressed, and then, the discontinuous jump of $\mathrm{d}M/\mathrm{d}H$ is observed at 5.2 T. This behavior obviously suggests that the ground state of this compound is of a gapped spin-singlet. If we assume that 1.52 K is enough low for the estimation of the spin-gap, we can recognize the jump of $\mathrm{d}M/\mathrm{d}H$ as the lowest excitation between singlet and triplet states. In this case, the gap energy was estimated to be $\Delta/k_{\mathrm{B}} \sim 7$ K from $H_{\mathrm{c1}} = 5.2$ T with using the most simplified relation of the spin-gap in the magnetic field, $\Delta(H) = \Delta - g\mu_{\mathrm{B}}H$. This value is different from $\Delta_{\mathrm{cal}}/k_{\mathrm{B}} = 15$ K estimated using the fitting parameters of the alternating model.[7] This may be ascribed to the effects of the interchain interaction $J_{3\mathrm{D}}$. On the other hand, the magnetic field 5.2 T can be regarded as the critical point between the paramagnetic and antiferromagnetic states at 1.52 K. We put this point on the H–T phase diagram shown in Fig. 6. The magnetization increases gradually over the whole external field range and saturates to about $1\,\mu_{\mathrm{B}}$/f.u. above 40 T, which is consistent with the $S = 1/2$ saturation moment. Furthermore, there is anomaly in $\mathrm{d}M/\mathrm{d}H$ at 36.8 T. This field corresponds to the critical field H_{c2} at 0 K.[6] In Fig. 3(b), we compare the experimental magnetization curve and that calculated by Bonner *et al.*[6] H_{c2} of 1DAFAHC model can be written as $H_{\mathrm{c2}} = |J_1 + J_2|/g\mu_{\mathrm{B}}$.[6] The value of H_{c2} was calculated to be 35.6 T with the values of J_1 and J_2 estimated above. The result well agrees with the experiment, while calculated $H_{\mathrm{c1}}(0)$ ($= \Delta_{\mathrm{cal}}/g\mu_{\mathrm{B}} = 11.1$ T) is different

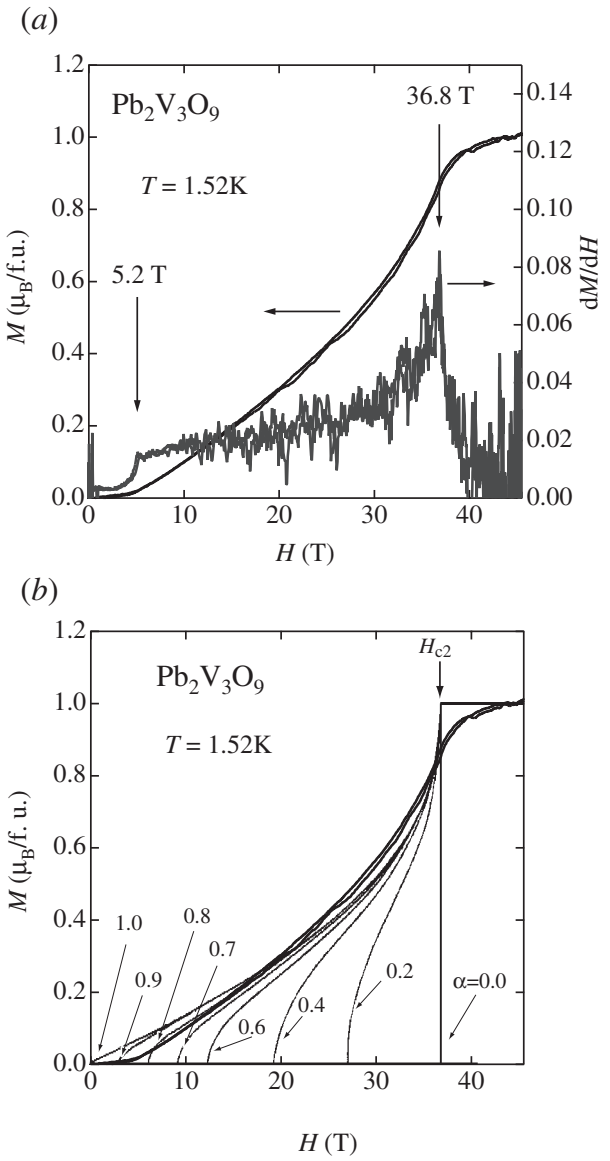

Fig. 3. (a) Magnetization curve of $Pb_2V_3O_9$ at 1.52 K. The left vertical axis indicates the magnetization, and the right one dM/dH. The critical field $H_{c1} = 5.2$ T at 1.52 K, corresponding to the spin-gap energy, is determined from the anomaly of the dM/dH curve. The magnetization curve saturates to 1 μ_B/f.u. at about 40 T. (b) The calculated magnetization curves for several fraction value α in the alternating model together with the observed one.[6] H_{c1} is the field where the curve intersects the horizontal axis of the graph and H_{c2} is the field where the curve saturates. The shape of the magnetization curve agrees qualitatively with the calculated curves. The difference in detail may come from the effects of J_{3D} left out of account in 1DAFAHC model.

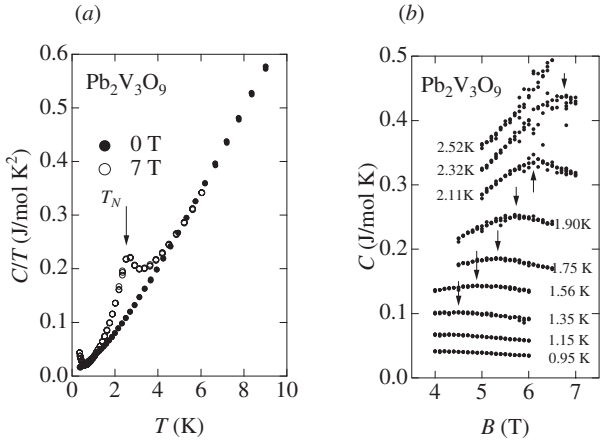

Fig. 4. (a) Temperature dependence of specific heat of $Pb_2V_3O_9$ measured under magnetic field of 0 T (solid circle) and 7 T (open circle). Increase of specific heat at low temperatures measured under 7 T is due to the nuclear spins under the magnetic field. (b) Field dependence of specific heat at several temperatures down to 0.35 K. There are cusp-like anomalies at the fields which we determined as H_c represented by allows.

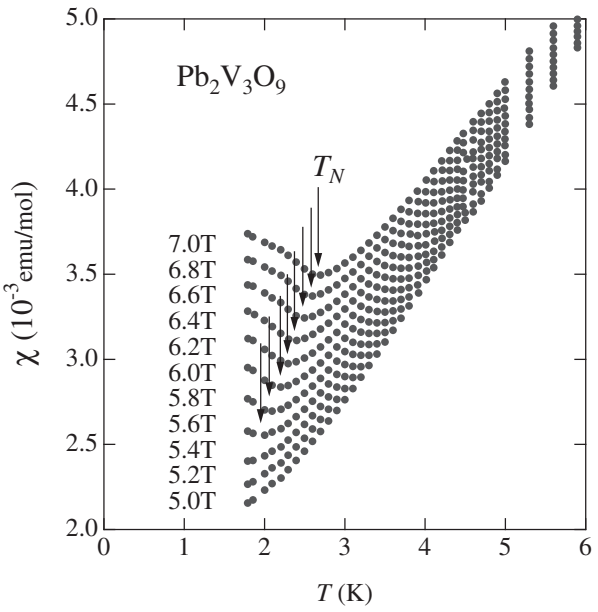

Fig. 5. Temperature dependence of χ measured under several fields. Above 5.6 T, a minimum of M/H was observed similar to the case of $TlCuCl_3$.[4]

from the experimental result.

Figure 4(a) is the temperature dependence of the specific heat C divided by T under 0 and 7 T. There are no tendencies of transition down to 0.35 K in C/T measured under $H =$ 0 T, consistent with the fact that the ground state of this compound is of spin-singlet. On the other hand, C/T under 7 T shows an obvious peak at 2.5 K, indicating an antiferromagnetic transition at the temperature, below which an antiferromagnetic long range ordering is realized in the spin triplet state. We determined the peak temperature of C/T as the Néel temperature T_N. There is a steep increase of C/T below 0.5 K measured under 7 T due to the contribution of the nuclear spins under external fields. Namely, we found a field-induced magnetic phase transition in $Pb_2V_3O_9$. We also measured the magnetic field dependence of the specific heat at several temperatures down to 0.35 K. The cusp-like anomaly indicating long range ordering was also observed and we determine the field where C takes maximum as H_c [Fig. 4(b)].

Figure 5 shows the temperature dependence of χ measured under several external fields down to 1.8 K. We observed a minimum of χ in external magnetic fields above 5.6 T. The temperature at which χ shows the minimum measured at 7 T almost coincides with the T_N determined by the specific heat measurement under 7 T. Therefore, we can consider that the anomalous behavior of χ is attributed to the field induced antiferromagnetic transition. As shown by

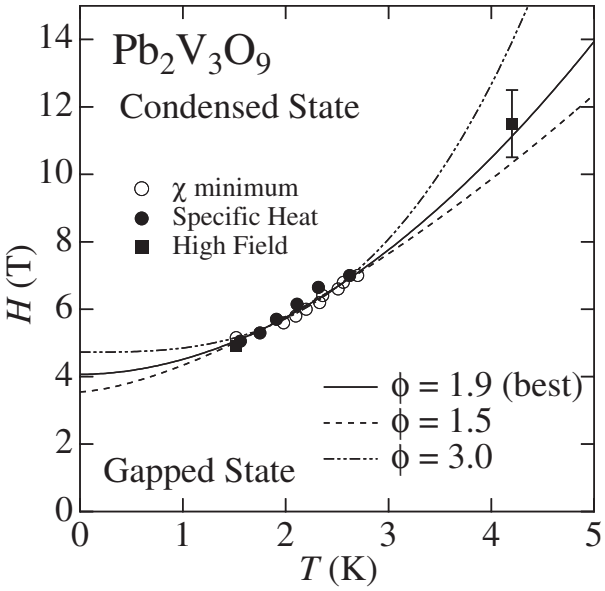

Fig. 6. H–T phase diagram of $Pb_2V_3O_9$. The fitting curve of the boundary using eq. (1) with the value $\phi = 1.9$ and $H_c(0) = 4.1\,\mathrm{T}$ is presented by solid line together with estimated curves with $\phi = 1.5$ (dotted line) and $\phi = 3.0$ (dashed two dots) for references.

arrows in the figure, T_N increases gradually as the field increases. The characteristic convex temperature dependence of χ below T_N was observed similar to the case of $TlCuCl_3$. One cannot expect convex behavior of χ without the consideration of the condensation of triplons. For example, the value of χ is known to be invariant below T_N on the basis of the mean field theory.[11] Hence, the minimum of χ can be comprehended in terms of the BEC state of triplons.[4] Therefore, the field induced magnetic ordering state in this system is thought to be just the BEC state of triplons.

In Fig. 6, we show the phase diagram, in which the phase boundary between paramagnetic and the BEC regions was estimated by the specific heat and magnetization measurements. From the least-square-fitting by eq. (1), we obtained $\phi = 1.9$ and $H_g = 4.1\,\mathrm{T}$ in the case of $Pb_2V_3O_9$. The power law behavior of the phase boundary is another feature of theory of triplon BEC: the critical exponent is predicted to be $\phi = 1.5$ by using Hartree–Fock approximation with simple quadratic dispersion.[4] On the other hand, $\phi = 2.2$ has been reported experimentally for $TlCuCl_3$.[4] The critical exponent $\phi = 1.9$ we obtained for $Pb_2V_3O_9$ also deviates from the theoretical prediction. Recently, some theories have been proposed in concerned with the critical exponent. Misguich and Oshikawa reobtained $\phi = 1.5$ with self-consistent Hatree–Fock–Popov calculations.[12] The region of $\phi = 1.5$ is limited to very low temperature region. Taking into account of a realistic dispersion of triplons of $TlCuCl_3$, they also reproduce the experimental phase boundary. The actual dispersion of triplons of $Pb_2V_3O_9$ remains to be studied. On the other hand, Crisan *et al.* have obtained the value of $\phi = 2$, which is in a better agreement with $\phi = 2.2$ on $TlCuCl_3$ system as well as the present case of $\phi = 1.9$, including fluctuation effect by the renormalization group method.[13] We need further experimental and theoretical studies of $Pb_2V_3O_9$ and in other isotropic spin-gap systems for understanding this phenomenon.

In summary, we observed a field-induced magnetic ordering as well as the gapped spin-singlet ground state in the 1D antiferromagnetic spin-chain compound $Pb_2V_3O_9$ with $S = 1/2$. Furthermore, our results suggest that the BEC of triplons is observable not only in weak coupled dimer systems but also in strongly coupled dimer system. From the H–T phase diagram, critical exponent seems to depend on the dimensionality (or dispersion) of the system as suggested from recent works. Further intensive experimental and theoretical works are needed for fully understanding of this phenomenon.

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