Single-Crystal Growth of Pb$_2$V$_3$O$_9$ and the Bose-Einstein Condensed State of Triplons Studied by Thermal Conductivity, Specific Heat and Magnetization Measurements

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Abstract. We have succeeded in growing large-size single crystals of the quasi-one-dimensional $S = 1/2$ spin-dimer system Pb$_2$V$_3$O$_9$ by the floating-zone method, and also investigated the thermal conductivity, specific heat and magnetization in magnetic fields. In high magnetic fields, it has been found that the suppression of the thermal conductivity by the application of magnetic field is relaxed. This behavior is caused by the enhancement of the thermal conductivity due to triplons and/or phonons owing to the extension of the mean free path of triplons and/or phonons in the Bose-Einstein condensed (BEC) state of field-induced triplons. We have estimated the critical field $H_c(T)$ between the BEC state of triplons and the gapped normal state from the thermal conductivity, specific heat and magnetization measurements and obtained the value of the critical exponent $\phi \sim 2.0$ in $[H_c(T) - H_c(0)] \propto T^\phi$ using $H_c(T)$'s at low temperatures.

1. Introduction

Recently, low-dimensional spin systems with the spin quantum number $S = 1/2$ has received great attention, for various phenomena of interest have been induced by the application of magnetic field or pressure. For example, Bose-Einstein condensation (BEC) of magnetic quasiparticles, namely, field-induced triplets (triplons) has been induced in the spin-dimer system TlCuCl$_3$ with a spin gap $\Delta \sim 7.5$ K [1] by the application of magnetic field above $\sim 5.5$ T [2]. The critical field $H_c(T)$ between the BEC state of triplons and the gapped normal state is expressed as

$$\left(\frac{g}{2}\right)[H_c(T) - H_c(0)] \propto T^\phi,$$

where $g$ is the $g$-factor and $\phi$ the critical exponent. The value of $\phi$ has theoretically been predicted to be 1.5 using Hartree-Fock calculations [2] and has experimentally been estimated to
be 1.5 using values of $H_c(T)$ obtained at very low temperatures down to 77 mK in TICuCl$_3$ [3]. In the BEC state of TICuCl$_3$, on the other hand, a drastic enhancement of the thermal conductivity has been observed [4], which is analogous to that in the superfluid state of liquid $^4$He [5].

Recently, a BEC state of field-induced triplons has been confirmed to appear in the $S = 1/2$ spin-dimer system Pb$_2$V$_2$O$_9$ which has one-dimensional bond-alternating spin-chains along the [1 0 1] direction [6]. The exchange interaction between adjacent spins is estimated as $J_1/k_B = -29.2$ K and $J_2/k_B = -19.3$ K from the magnetic susceptibility measurements [7] and the spin gap is estimated as $\Delta \sim 7$ K from the magnetization curve [6].

In this paper, we investigate the thermal conductivity in the BEC state of Pb$_2$V$_2$O$_9$ and the phase boundary between the BEC state and the gapped normal state. First, we have attempted to grow large-size single-crystals of Pb$_2$V$_2$O$_9$ by the floating-zone (FZ) method, because precise measurements of thermal conductivity need a large-size single-crystal. Then, we have measured the thermal conductivity, specific heat and magnetization of the obtained single-crystals.

2. Experimental

Thermal conductivity measurements were carried out in magnetic fields up to 14 T by the conventional steady-state method. The specific heat was measured in magnetic fields up to 9 T by the thermal relaxation technique (Quantum Design, Model PPMS). The magnetization curve in magnetic fields up to 18 T was measured using an extraction-type magnetometer [8].

3. Results and Discussion

In order to prepare a feed rod for the FZ growth, first, we prepared polycrystalline powders of Pb$_2$V$_2$O$_7$ by the solid-state reaction method. After pulverization, the prefired powders of Pb$_2$V$_2$O$_7$ were mixed with VO$_2$ powders in the molar ratio of Pb$_2$V$_2$O$_7$ : VO$_2$ = 1 : 1. The fired powders were pulverized and isostatically cold-pressed at 600 bar into a rod of 7 mm in diameter and $\sim 120$ mm in length. Then, the rod was sintered at 500°C in Ar for 24 h. Using the sintered feed rod, the FZ growth was carried out by the twice-scanning technique in an infrared heating furnace equipped with a double ellipsoidal mirror. A high-density premelted feed rod was prepared through the first scan. In the first scan, the molten zone was scanned at a speed of $\sim 20$ mm/h under flowing Ar of 4 atm. Next, the second scan, namely, an usual growing procedure was carried out using the premelted feed rod at the growth rate of 1.0 mm/h under flowing Ar of 4 atm.

Although the FZ growth was not so easy because of the very small viscosity of the liquid in the molten zone, we have managed to succeed in growing crystals of Pb$_2$V$_2$O$_9$. The size of the single domain is the order of $\sim 5 \times 5 \times 10$ mm$^3$. The grown crystals have been confirmed by the powder x-ray diffraction to be of the single phase of Pb$_2$V$_2$O$_9$ without any impurity phases. The chemical composition has been confirmed by the inductively coupled plasma optical emission spectrometry (ICP-OES) to coincide with the nominal composition. The details of the single crystal growth will be described in a separate paper [9].

Figure 1 (a) shows the temperature dependence of the thermal conductivity along the [7 0 5] direction which is $79^\circ$ tilted from the spin-chain direction, $\kappa_{[\bar{7} 0 5]}$, in magnetic fields parallel to the heat current. The $\kappa_{[\bar{7} 0 5]}$ exhibits a peak due to the contribution of phonons around 8 K in zero field. The peak is suppressed by the application of magnetic field, which is interpreted as being due to the enhancement of the phonon-spin scattering owing to the suppression of the spin gap by the application of magnetic field. The temperature dependence of $\kappa_{[\bar{7} 0 5]}(H)/\kappa_{[\bar{7} 0 5]}(0)$ is shown in Fig. 1 (b) in order to see the change of $\kappa_{[\bar{7} 0 5]}(H)$ in the BEC state clearly. It is found that $\kappa_{[\bar{7} 0 5]}(14\ T)/\kappa_{[\bar{7} 0 5]}(0)$ exhibits a kink at 4.2 K to be constant at very low temperatures, indicating that the decrease in $\kappa_{[\bar{7} 0 5]}(14\ T)$ with decreasing temperature is relaxed at low temperatures below 4.2 K. The relaxation of the decrease is also observed in the magnetic-field dependence of $\kappa_{[\bar{7} 0 5]}$ at 3.0 K, as shown in the inset of Fig. 1 (a). It is found that the decrease
κ-triplons, and the BEC state of triplons as in the case of TlCuCl
in the superfluid state of liquid 4He [10], it is possible that both the thermal conductivity due to
triplons, κ_{triplon}, and that due to phonons, κ_{phonon}, are enhanced owing to the extension of the mean
free path of triplons and phonons, respectively, because condensed triplons in the BEC
state do not contribute to the scattering. At present, it is hard to determine which of
κ_{triplon} and κ_{phonon} is dominant in the enhancement of the thermal conductivity in the BEC state. The
thermal conductivity measurement along the spin-chain direction may be significant, because
a very large enhancement of the thermal conductivity in the BEC state is expected if κ_{triplon} is
more dominant than κ_{phonon}. In other words, the small enhancement of κ_{[\bar{7} 0 5]} in the BEC state
may be due to the direction of the measurements being nearly perpendicular to the spin-chain
direction.

We have also measured the temperature dependence of the specific heat in magnetic fields
parallel to the three principal axes. A λ-type peak has been observed at the temperature
corresponding to H_c(T) and reduced and shifted to the lower temperature side with increasing
field. The peak temperature has nearly been independent of the field direction. Therefore, it
has been found that the anisotropy of H_c(T) is very small. Furthermore, we have measured the
magnetization curve in magnetic fields parallel to the b-axis at various temperatures. Values of
the magnetization have been very small up to H_c(T) and then increased rapidly with increasing

Figure 1. Temperature dependences of (a) the thermal conductivity, κ, and (b) κ(H)/κ(0) along the [\bar{7} 0 5] direction in
magnetic fields parallel to the heat current Q. The inset of Fig. (a) shows the field dependence of κ at 3.0 K. Arrows indicate
transitions to the BEC state.

Figure 2. Phase boundary between the Bose-Einstein condensed state of triplons and the gapped normal state in Pb_2V_3O_9, H_c(T),
determined from the present thermal conductivity, specific heat, magnetization measurements
in magnetic fields. Values of H_c(T) determined from the specific heat [6], magnetization [6, 11],
NMR [11] and ESR [12] measurements using polycrystalline samples are also plotted for reference.
field. Values of $H_c(T)$ have been determined from the derivative of the magnetization in the same way as used by Waki et al. [6].

Figure 2 shows values of $H_c(T)$ obtained from the thermal conductivity, specific heat and magnetization measurements. All values are well located on the phase-boundary line between the BEC state of triplons and the gapped normal state obtained from former various measurements using polycrystalline samples [6, 11, 12]. In order to determine the value of $\phi$, we have fitted values of $H_c(T)$ obtained from our magnetization measurements at low temperatures between 0.5 K and 2.5 K to Eq. (1). It has turned out that the value of $\phi$ is around 2.0 and larger than 1.5 obtained from Hartree-Fock calculations [2]. In order to obtain the precise value of $\phi$ in Pb$_2$V$_3$O$_9$, values of $H_c(T)$ at very low temperatures below 0.5 K may be necessary as in the case of TlCuCl$_3$ [3].

4. Summary

We have succeeded in growing large-size single-crystals of Pb$_2$V$_3$O$_9$ by the FZ method. From the thermal conductivity measurements in magnetic fields, it has been found that the thermal conductivity is enhanced in the BEC state of triplons in high magnetic fields at low temperatures. The enhancement is attributed to the enhancement of $\kappa_{\text{triplon}}$ and/or $\kappa_{\text{phonon}}$ owing to the extension of the mean free path of triplons and/or phonons in the BEC state of triplons. Moreover, we have estimated values of $H_c(T)$ from the thermal conductivity, specific heat and magnetization measurements and obtained the value of $\phi \sim 2.0$ using $H_c(T)$’s at low temperatures between 0.5 K and 2.5 K.

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