Anisotropic Behavior of Thermal Conductivity in the Bose-Einstein Condensed State of the Bond-Alternating Spin-Chain System Pb$_2$V$_3$O$_9$

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Abstract. We have systematically measured the thermal conductivity along the [101], [10$ar{1}$] and b directions, $\kappa_{[101]}$, $\kappa_{[10\bar{1}]}$ and $\kappa_b$, respectively, of the $S = 1/2$ bond-alternating spin-chain system Pb$_2$V$_3$O$_9$ in magnetic fields parallel and perpendicular to the heat current. It has been found that $\kappa_{[101]}$ along the spin chains is markedly enhanced in the BEC state, which has been concluded to be due to the enhancement of the thermal conductivity due to triplons. Furthermore, it has been found that the enhancement of $\kappa_{[101]}$ in the BEC state is more marked in magnetic fields parallel to the [101] direction than perpendicular to the [101] direction. The BEC state may be weakened or broken in magnetic fields perpendicular to the [101] direction on account of the breaking of the rotational symmetry.

1. Introduction

Thermal conductivity is recognized as a good probe detecting a change of the spin state in a spin system, because the scattering rate of heat carries, such as electrons, phonons and magnetic excitations, is affected sensitively by the change of the spin state. For example, a drastic enhancement of the thermal conductivity has been observed in the Bose-Einstein condensed (BEC) state of field-induced magnetic excitations, namely, triplons in the three-dimensional (3D) spin-dimer system TlCuCl$_3$ with the spin quantum number $S = 1/2$ [1], which is analogous to that observed in the BEC superfluid state of liquid $^4$He [2]. However, it has not yet been clarified whether the enhancement in the BEC state is due to thermal conductivity due to phonons, $\kappa_{\text{phonon}}$, or that due to triplons, $\kappa_{\text{triplon}}$.

The compound Pb$_2$V$_3$O$_9$ contains both two nonmagnetic V$^{5+}$ ions located in VO$_4$ tetrahedra and one V$^{4+}$ ion with $S = 1/2$ in VO$_6$ octahedra in the unit cell. As shown in Fig. 1, VO$_6$ octahedra are connected with each other by sharing an oxygen at the corner along the [101] direction, forming a $S = 1/2$ bond-alternating spin-chain. It has been reported that the ground state is of spin-singlets with a spin gap $\Delta \sim 7$ K and that the spin gap disappears by the application of magnetic field, followed by the appearance of a BEC state of triplons [3].

The anisotropy of the magnetic interaction of the one-dimensional (1D) spin system Pb$_2$V$_3$O$_9$ is stronger than that of the 3D spin system TlCuCl$_3$. Considering that the value of $\kappa_{\text{triplon}}$ is related to the magnitude of the magnetic interaction and that $\kappa_{\text{phonon}}$ is comparatively isotropic, the origin of the enhancement of the thermal conductivity in the BEC state of field-induced...
triplons might be understood in terms of the anisotropy of the thermal conductivity in the BEC state of Pb$_2$V$_3$O$_9$. Therefore, we have systematically measured the thermal conductivity along the [101], [010] and $b^*$ directions, $\kappa_{[101]}$, $\kappa_{[010]}$ and $\kappa_{b^*}$, respectively, of single-crystal Pb$_2$V$_3$O$_9$ in magnetic fields parallel to the [101], [010] and $b^*$ directions, $H_{[101]}$, $H_{[010]}$ and $H_{b^*}$, respectively. The preliminary results have already been reported [4, 5].

2. Experimental

Large single-crystals of Pb$_2$V$_3$O$_9$ were grown by the floating-zone method [4]. Thermal conductivity measurements were carried out by the conventional steady-state method in magnetic fields up to 14 T.

3. Results and Discussion

Figures 2(a)–(c) show the temperature dependence of $\kappa_{[101]}$, $\kappa_{[010]}$ and $\kappa_{b^*}$ in zero field and in a magnetic field of 14 T. It is found that every thermal conductivity exhibits a peak around 10 K in zero field. The peak is regarded as being due to the enhancement of $\kappa_{\text{photon}}$ on account of the suppression of both phonon-phonon scattering and phonon-triplon scattering, because $\kappa_{\text{triplon}}$ is usually very small in zero field at low temperatures in spin-gap systems [1]. Here, it is noted that the magnitude of the thermal conductivity in zero field is a little different sample by sample, even though the heat-current direction is the same. This may be due to the difference of the degree of the oxidation of samples during the sample setting to the heat sink using indium solder and so on, because the oxidation of Pb$_2$V$_3$O$_9$ is guessed to change V$^{4+}$ ions to V$^{5+}$ ions so that spin defects and local lattice distortions are introduced into samples, leading to the suppression of the thermal conductivity.

By the application of magnetic field, the peak is markedly suppressed, which is interpreted as being due to the enhancement of the phonon-triplon scattering because of the reduction of the spin gap. Neither marked enhancement as observed in TlCuCl$_3$ [1] is observed at a glance in $\kappa_{[101]}$, $\kappa_{[010]}$ nor $\kappa_{b^*}$ in the BEC state of Pb$_2$V$_3$O$_9$. In order to see the field effect in detail, the temperature dependence of the thermal conductivity in 14 T divided by that in zero field, $\kappa(14T)/\kappa(0)$, is shown in Figs. 2(d)–(f). It is found that the value of $\kappa(14T)/\kappa(0)$ decreases with decreasing temperature due to the formation of the spin gap in zero field. Furthermore, it is found that every $\kappa(14T)/\kappa(0)$ clearly exhibits a kink at a low temperature around 4 K corresponding to the BEC transition temperature shown by arrows in Figs. 2(d)–(f) [3, 4, 6, 7]. This indicates that the BEC transition temperature is independent of the applied-field direction and that the thermal conductivity is more or less enhanced at low temperatures in the BEC state. The former is reasonable, because Pb$_2$V$_3$O$_9$ is regarded as a Heisenberg spin system without any magnetic easy axis. The enhancement of $\kappa_{[101]}(14T)/\kappa_{[101]}(0)$ in the BEC state is much more marked than those of $\kappa_{[010]}(14T)/\kappa_{[010]}(0)$ and $\kappa_{b^*}(14T)/\kappa_{b^*}(0)$, so that $\kappa_{[101]}(14T)/\kappa_{[101]}(0)$ shows up-turn below about 4 K.

The enhancement of the thermal conductivity in the BEC state is interpreted as follows. In the BEC state of field-induced triplons, both the mean free path of phonons and that of uncondensed triplons increase, because neither phonons nor uncondensed triplons are scattered

Figure 1. Crystal structure of Pb$_2$V$_3$O$_9$ viewed from the $b^*$-axis.
The slow decrease of $\kappa_{[101]}$ in $H_{[101]}$ and $H_{b^*}$ may be understood to be due to breaking or weakening of the BEC state of triplons on account of the breaking the rotational symmetry by the application of $H_{[101]}$ and $H_{b^*}$ for the rotational invariance is necessary for the conservation of the number of triplons in magnetic fields [9]. In fact, such breaking of the BEC state depending on the applied-field direction has been observed in the 1D spin-gap system $(\text{CH}_3)_{2}\text{CHNH}_2\text{CuCl}_3$ (IPACuCl₃)[10]. The temperature dependence of the magnetization of Pb₂V₃O₉ in high fields

**Figure 2.** Temperature dependence of the thermal conductivity, $\kappa$, along the [101], [101] and $b^*$ directions of Pb₂V₃O₉, $\kappa_{[101]}$, $\kappa_{[10\bar{1}]}$ and $\kappa_{b^*}$, respectively, in zero field and in a magnetic field of 14 T parallel to the (a) [101], (b) [101] and (c) $b^*$ directions. Temperature dependence of $\kappa(14\text{T})/\kappa(0)$ along the [101], [101] and $b^*$ directions of Pb₂V₃O₉ in magnetic fields parallel to the (d) [101], (e) [101] and (f) $b^*$ directions. Arrows indicate the BEC transition temperature in 14 T.
above 9 T along the $b$-axis (1.2° tilted from the $b^*$-axis) strongly supports the breaking or weakening of the BEC state as well [11]. Therefore, it is understood that $\kappa_{\text{triplon}}$ is markedly enhanced when the field-induced magnetically ordered state is regarded as a BEC state of triplons, otherwise the enhancement of $\kappa_{\text{triplon}}$ is little. As for $\kappa_{\text{phonon}}$, it is understood that $\kappa_{\text{phonon}}$ is a little enhanced in the field-induced magnetically ordered state owing to the suppression of the phonon-triplon scattering whether it is regarded as a BEC state or not.

4. Conclusions
We have measured temperature and magnetic field dependences of $\kappa_{[101]}$, $\kappa_{[01]}$ and $\kappa_{b^*}$ of Pb$_2$V$_3$O$_9$ in $H_{[101]}$, $H_{[01]}$ and $H_{b^*}$. Only $\kappa_{[101]}(14T)/\kappa_{[101]}(0)$ has been found to be markedly enhanced in the BEC state at low temperatures, suggesting that $\kappa_{\text{triplon}}$ contributes to $\kappa_{[101]}$ along the spin chains. As for the field dependence of $\kappa_{[101]}$ in the BEC state at 3 K, furthermore, it has been found that $\kappa_{[101]}$ markedly increases with increasing $H_{[101]}$, while $\kappa_{[101]}$ slowly decreases with increase $H_{[01]}$ and $H_{b^*}$. The slow decrease of $\kappa_{[101]}$ in $H_{[01]}$ and $H_{b^*}$ may be due to breaking or weakening of the BEC state of triplons on account of the breaking of the rotational symmetry. Additionally, it is concluded that the drastic enhancement of the thermal conductivity observed in the BEC state of triplons in TiCuCl$_3$ is probably due to the contribution of $\kappa_{\text{triplon}}$.

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