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Anomalous thermal conductivity of NaV$_2$O$_5$ as compared to conventional spin-Peierls system CuGeO$_3$

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A huge increase of thermal conductivity $\kappa$ is observed at the phase transition in stoichiometric NaV$_2$O$_5$. This anomaly decreases and gradually disappears with deviation from stoichiometry in Na$_{1-x}$V$_2$O$_5$ ($x = 0.01, 0.02, 0.03,$ and $0.04$). This behavior is compared with that of pure and Zn-doped CuGeO$_3$ where only modest kinks in the $\kappa(T)$ curves are observed at the spin-Peierls transition. The change of $\kappa$ at critical temperature $T_c$ could be partially attributed to the opening of an energy gap $\Delta$ in the magnetic excitation spectrum excluding the scattering of thermal phonons on spin fluctuations. However, the reason for such a strong anomaly in the $\kappa(T)$ may lie not only in the different energy scales of CuGeO$_3$ and NaV$_2$O$_5$, but also in the different character of the phase transition in NaV$_2$O$_5$ which can have largely a structural origin, e.g. connected with the charge ordering.
between these layers. In the former non-centrosymmetric structure, there exists alternating chains of nonmagnetic V$^{4+}$ ions and magnetic V$^{4+}$ ones (3d$^1$, S = 1/2) aligned along the b axis (see e.g. Fig. 1 of Ref. [2]). In the latter structure, all the V sites are crystallographically equivalent, which results formally in a random distribution of the V$^{4+}$ and V$^{5+}$ ions, or in a localization of electrons on V-O-V molecular orbitals on the rungs of the ladders running along the b axis (see e.g. Fig. 1 of Ref. [13]). In such a situation a one-dimensional magnetic behavior does not come about straightforwardly but can still be justified [13-15].

In order to clarify a picture of the phase transition in NaV$_2$O$_5$, more experimental data are necessary. One of the few experimental techniques not yet applied to the study of SP transitions in metal oxides is the measurement of thermal conductivity which can provide useful information on the interaction of elementary excitations in these compounds.

In this letter we report on the first, to the best of our knowledge, such measurements, which show a surprisingly strong effect in NaV$_2$O$_5$, in comparison with the rather weak anomaly observed in CuGeO$_3$. A possible interpretation of this effect is considered below and it is concluded that the nature of the phase transition in NaV$_2$O$_5$ may be more complicated than previously assumed.

Single crystals of CuGeO$_3$ and Cu$_{0.58}$Zn$_{0.42}$GeO$_3$ were grown in Paris University by a floating zone method [16]. Single crystals of stoichiometric NaV$_2$O$_5$ were grown in Tokyo University by the self-flux method [17]. Single crystals of non-stoichiometric Na$_{1-x}$V$_2$O$_5$ (x = 0.01, 0.02, 0.03, and 0.04) were prepared by heating a small crystal of stoichiometric NaV$_2$O$_5$ embedded in a large quantity of Na$_{1-x}$V$_2$O$_5$ powder in an evacuated silica tube at 650°C for one week. The non-stoichiometric samples of Na$_{1-x}$V$_2$O$_5$ contain vacancies on the Na sites. Typical dimensions of the crystals used in the thermal conductivity measurements were 0.2 x 0.8 x 4.0 mm$^3$. The largest dimension coincided with the dimerization axis, i.e. the c axis in the case of CuGeO$_3$, and the b axis in the case of NaV$_2$O$_5$. The smallest dimension coincided with the a axis in the layered structure of CuGeO$_3$ and c axis in the layered structure of NaV$_2$O$_5$. In most cases, measurements were performed in the direction of dimerization, but in CuGeO$_3$ thermal conductivity was measured also along the b axis. The measurements were performed by the longitudinal steady-state four probe method [18] with a temperature gradient equal to 2% of the current temperature. The sample holder, surrounded by a special shell to suppress the thermal radiation, was placed into the vacuum chamber evacuated to better than 10$^{-6}$ bar. The sample temperature and the temperature gradient were stabilized to better than 0.01% by an Oxford intelligent temperature controller with calibrated "Allen-Bradley" carbon resistors. Due to the relatively small dimensions of the samples the error in the determination of the absolute values of thermal conductivity was not better than 10%, while the precision on the thermal conductivity variations was about 1.5%.

The experimental results obtained in the c and b directions for pure CuGeO$_3$ and for the Zn-doped sample are shown in Fig. 1. A broad phonon maximum of $\kappa$ is observed at $T_c = 33.3$ K in the c direction, while it is not well pronounced in the b direction. The absolute value of $\kappa$ in the b direction is apparently three times lower than that in the c direction. The kinks on the $\kappa(T)$ curves are evident at the temperature of the SP transition. The SP transition temperature in the Zn-doped sample is reduced to $T_e = 10.6$ K to be compared to that of the pure sample $T_c = 14.2$ K. The absolute value of $\kappa$ at the SP transition in the doped sample is significantly smaller than that in the pure sample.

The thermal conductivity of stoichiometric NaV$_2$O$_5$ exhibits a much more dramatic variation in the temperature range studied. As shown in Fig. 2, the thermal conductivity exhibits a broad maximum at $T \approx 70$ K and decreases upon approaching the SP transition. At $T_c$ a sharp upturn of $\kappa$ occurs so that a five times increase of thermal conductivity accompanied by a subsequent decrease of $\kappa$ upon cooling to liquid helium temperature takes place. A behavior similar to the one described above can be seen in non-stoichiometric samples of Na$_{1-x}$V$_2$O$_5$ ($x = 0.01, 0.02, 0.03,$ and 0.04) with the progressively less pronounced maximum below $T_c$, as shown in Fig. 3. The position of the low temperature maximum remains unchanged in non-stoichiometric samples but absolute values of $\kappa$ gradually decrease with $x$. Certain variation in the high temperature slopes and the vertical shift between the curves obtained for 0 and 1% and the curves for 2, 3 and 4% Na deficiency can be tentatively ascribed to a variation in the crystals morphology. These crystals can be easily cleaved perpendicular to the c axis, resulting in an uncontrolled extra scattering of the phonons on planar defects. The spin-Peierls transition temperatures in Na$_{1-x}$V$_2$O$_5$ determined from the positions of the minimum on the $\kappa(T)$ curves are shown in Fig. 4, where the solid curve is drawn as a guide for an eye. The suppression of $T_c$ by the Na-deficiency was observed earlier in X-ray critical scattering measurements [19].

Since no quantitative treatment of the transport phenomena for the spin-Peierls systems exists, we applied the Boltzmann equation for the analysis of the experimental data. In this approach the phonon thermal conductivity $\kappa \sim v/C$ is determined by the sound velocity $v$, the mean free path of phonons $l$, and the specific heat $C$ which depends on the number of elementary excitations. The interactions of the phonon and the spin subsystems can be taken into account through the variation of the phonons mean free path. In the absence of these interactions, the mean free path of the phonons increases upon cooling and eventually saturates while their number decreases. These opposite tendencies result in a phonon maximum $T_{\max}$ on the $\kappa(T)$ curves. The estimated phonon mean free path in CuGeO$_3$ is still much smaller than the sample dimensions; we believe that this is caused by the phonon scattering on planar defects.
in the layered structure of this compound. The difference in the absolute values of the thermal conductivity in the $b$ and the $c$ directions in CuGeO$_3$ can naturally be attributed to a factor three difference in ultrasonic velocities, i.e. $2.7\times10^3$ m/sec in the $b$ direction and $8.0\times10^3$ m/sec in the $c$ direction [20]. On the other hand, the small thermal conductivity value of in the Cu$_{38}$Zn$_{62}$GeO$_3$ sample as compared with that of the pure CuGeO$_3$ sample reflects the increased number of scattering centers in the doped sample.

Anomalies observed in the temperature dependence of the thermal conductivity at the spin-Peierls transition can be naturally explained with the change of the crystal lattice and with the formation of the energy gap in the magnetic excitation spectrum. The mutual positions of the temperatures of the phonon maximum $T_m$ and of the spin-Peierls transition $T_x$, is of crucial importance for the analysis of these anomalies. The phonon maximum in CuGeO$_3$ is reached at $T_m > T_x$. In this case a possible decrease of the phonon scattering on spin fluctuation at $T_x$ cannot significantly influence the thermal conductivity, because the phonon mean free path is already large, and only modest kinks on the $\kappa(T)$ are observed. From the behavior of Na$_3$V$_2$O$_5$ we have to conclude that the situation here is exactly opposite. If the maximum of $\kappa$ at 70 K would have the same origin, we would not be able to explain such a strong increase of $\kappa$ below $T_x$. Therefore we have to assume that the decrease of $\kappa$ below 70 K in Na$_3$V$_2$O$_5$ is of a different nature, and most probably can be explained by the enhancement of phonon scattering on approaching the phase transition. The ordering occurring below $T_x$ apparently switches off this extra scattering and leads to a huge increase of the thermal conductivity. No variation of the sound velocity at $T_x$ can explain the observed behavior of the thermal conductivity in Na$_3$V$_2$O$_5$. While no data for the absolute value of the sound velocity are available, a longitudinal velocity variation $\Delta v/v \sim 10^{-3}$ was observed at $T_x$ preceded by a precursor effects observable below 70 K [21].

Several factors may play a role in the much stronger enhancement of the thermal conductivity below $T_x$ in Na$_3$V$_2$O$_5$ as compared to CuGeO$_3$. The spin gap is much larger in Na$_3$V$_2$O$_5$ ($\sim 100$ K vs $\sim 25$ K in CuGeO$_3$). Opening of this gap switches off spin-phonon scattering for phonons with frequencies less that $\Delta$. A four times larger spin gap in Na$_3$V$_2$O$_5$ implies that much more phonons will now strongly contribute to thermal conductivity below $T_x$. This picture could, in principle, have allowed also to explain the behavior of the thermal conductivity of Na$_3$V$_2$O$_5$ as a function of the deviation from stoichiometry. Magnetic measurements show that, in contrast with the relatively small suppression of $T_x$ with $x$, the drop of magnetic susceptibility below $T_x$ is strongly reduced and for $x = 0.03 - 0.04$ it nearly vanishes. This shows that the spin gap is now, to a large extent, filled by magnetic excitations. Correspondingly, the phonon-phonon scattering is being restored, which suppresses the increase of $\kappa$ below $T_x$ in non-stoichiometric samples.

However, the comparison with CuGeO$_3$ shows that pure spin-phonon scattering is hardly sufficient to explain huge increase of $\kappa$ observed. Magnetoelastic coupling in Na$_3$V$_2$O$_5$ is not strong enough, which follows e.g. from the very weak dependence of $T_x$ on magnetic field [23]. We believe that the huge increase of the thermal conductivity in Na$_3$V$_2$O$_5$ can be related to the specific features of the phase transition in this compound. If the crystal structure above $T_x$ is indeed that obtained in recent studies [11-13], all V ions are on the average equivalent, i.e. the V$^{4+}$ ions. Such a state can be visualized as the (dynamic) random mixture of V$^{4+}$ and V$^{5+}$. If slow enough, these charge fluctuations can strongly enhance phonon scattering and reduce thermal conductivity similar to a situation in glasses. The phase transition may then be accompanied, or even caused, by the charge ordering [22] at which this extra scattering mechanism is switched off. The opening of a spin gap may then be not so much a driving force but a consequence of this ordering. The transition from the disordered glass-like phase to an ordered one could explain the strong enhancement of the thermal conductivity below $T_x$. This picture can also explain the observation [23] that the total entropy of the transition in Na$_3$V$_2$O$_5$ is larger than the pure spin one.

Although our measurements do not allow to draw a final conclusion about the microscopic picture of the changes occurring at the phase transition in Na$_3$V$_2$O$_5$, the qualitative difference observed in the behavior of CuGeO$_3$ and Na$_3$V$_2$O$_5$ can be taken as an evidence that the nature of the transition in Na$_3$V$_2$O$_5$ is more complicated than in CuGeO$_3$ and most probably directly involves lattice and charge degrees of freedom, e.g. in a form of charge ordering. Further experiments, especially neutron scattering, should shed light on the microscopic picture of the spin-Peierls transition in Na$_3$V$_2$O$_5$ and should clarify the nature of the strong anomaly in the thermal conductivity of Na$_3$V$_2$O$_5$ reported in this letter.

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After submission of this paper the results of NMR studies of NaV$_2$O$_5$ became available (T. Ohama et al, Submitted to Phys. Rev. Lett.), which show that there appear inequivalent V ions at T<T$_c$, so that most probably indeed a charge ordering occurs at T$_c$ in NaV$_2$O$_5$.

B. Buchner, private communication.

FIG. 1. Temperature dependences of thermal conductivity in pure and Zn-doped CuGeO$_3$.

FIG. 2. Temperature dependences of thermal conductivity $\kappa$ and of magnetic susceptibility $\chi$ in stoichiometric NaV$_2$O$_5$.

FIG. 3. Temperature dependences of thermal conductivity in Na$_{1-x}$V$_2$O$_5$ ($x = 0, 0.01, 0.02, 0.03$, and $0.04$).

FIG. 4. Critical temperatures of the spin-Peierls transition in Na$_{1-x}$V$_2$O$_5$ as obtained from the thermal conductivity data. The solid curve is drawn as a guide for an eye.
$\kappa (W \, m \, K)$

$T (K)$

- $\text{Cu}_{0.98} \text{Zn}_{0.02} \text{GeO}_3$, $\text{c axis}$
- $\text{CuGeO}_3$, $\text{b axis}$
- $\text{CuGeO}_3$, $\text{c axis}$
\( \kappa \) (W/m K)

\( \chi \) (10^4 emu / V+mol)

\( T \) (K)

\( \text{NaV}_2\text{O}_5 \)
$\text{Na}_{1-x} \text{V}_2 \text{O}_5$

$T_c (K)$ vs $x$ (\%)