

Long range and short range magnetic order in new compound NaVGe_2O_6

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The new metaloxide pyroxene compound NaVGe_2O_6 containing isolated edge-sharing VO_6 ($S = 1$) chains undergoes a transition into a long range antiferromagnetic state at $T_N = 16$ K. The broad maximum in the temperature dependence of magnetic susceptibility at $T_M = 26$ K indicates the low-dimensional character of magnetic subsystem. Even though the antiferromagnetic ordering is accompanied by a sharp peak of specific heat, significant magnetic entropy is released above the Neel temperature.

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The search for compounds containing integer or half-integer spin chains is motivated by their intriguing properties at low temperatures. The magnetic excitation spectrum of integer spin chains is gapped, so that the lowest lying excited states are separated by a finite energy gap from the ground state [1]. This is in contrast to the case of half-integer spin chains where the magnetic excitation spectrum is gapless [2]. The gap in the magnetic excitation spectrum of the half-integer spin chain can be introduced through the dimerization of uniform chains. This dimerization known as the spin-Peierls transition occurs due to magnetoelastic coupling in an intrinsically unstable quantum spin chain [3]. Recently, it was conjectured [4] that the LiVGe_2O_6 pyroxene represents a remarkable example of a compound that combines the properties of both integer and half-integer quantum spin chains. The idea was that an anomalously large biquadratic exchange interaction closes the Haldane gap in the $S = 1$ spin chain and this now gapless integer spin chain undergoes a spin-Peierls phase transition. However this idea was not supported by neutron diffraction experiment, it was concluded that LiVGe_2O_6 undergoes at low temperatures a transition into a commensurate antiferromagnetic long range ordered state [5]. The realization of either spin-Peierls or Neel ground state depends on tiny variations of structure and magnetic subsystem parameters. These variations occur with isovalent chemical substitutions within a given structure. Here, we present the results of an investigation of structural, magnetic and thermal properties of new member of the pyroxene compounds family NaVGe_2O_6 .

The crystal structure of NaVGe_2O_6 , shown in Fig.1, is monoclinic with a space group $P2_1/c$ [6]. This structure contains isolated chains of VO_6 edge-sharing octa-

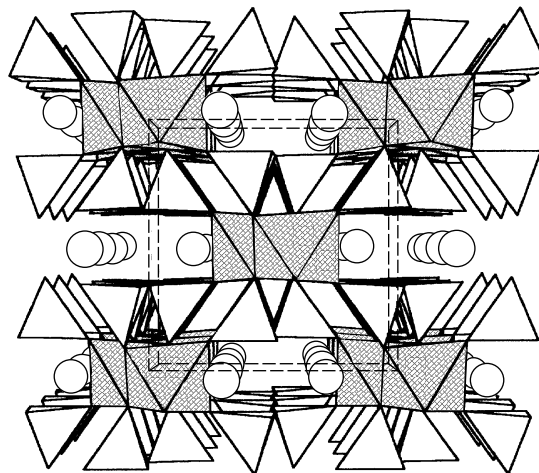


Fig.1. The crystal structure of NaVGe_2O_6 pyroxene. The unit cell is shown by dotted lines, Na^+ ions are represented by dark circles, V^{3+} ions are situated within grey VO_6 octahedrons, Ge^{4+} ions are situated within light-colored GeO_4 tetrahedrons

hedra running along the c -axis. These chains are separated by the double chains of distorted GeO_4 tetrahedra. In the crystal structure of pyroxenes the valence state of vanadium is 3+ and V ions have the integer spin $S = 1$.

The solid state synthesis of NaVGe_2O_6 was carried out at 900°C in an evacuated silica tube several days from the stoichiometric mixture of $\text{Na}_4\text{Ge}_9\text{O}_{20}$, GeO_2 , V and V_2O_3 . $\text{Na}_4\text{Ge}_9\text{O}_{20}$ was prepared by heating mixtures of NaCO_3 and GeO_2 at 800°C in air. An olive

Structural, thermal and magnetic parameters of NaVGe₂O₆

Structural parameters	a , Å	b , Å		c , Å		β'	
	9.62(5)	8.72(3)		5.28(8)		106.8(7)	
Thermal parameters	β , J/mol · K ⁴	E_1 , K	E_2 , K	E_3 , K	Q , J/mol	ΔS_{magn} , J/mol · K	ΔS_{AF} , J/mol · K
	$3.13 \cdot 10^{-3}$	166	417	956	117	9	4.1
Magnetic parameters	Θ , K	μ_{eff} , μ_B	T_M , K	T_N , K	J_{\parallel} , K	J_{\perp} , K	J_{\perp}/J_{\parallel}
	-70	3.16	26	16	20	2.2	0.11

color product of synthesis was obtained. The purity and phase composition of the sample were checked by powder X-ray diffraction at room temperature. It was confirmed that the powder was single phase with the crystal structure of pyroxene. The crystal lattice parameters of NaVGe₂O₆ at room temperature are given in Table.

The magnetization in the range 2–350 K was measured by a “Quantum Design” SQUID-magnetometer at 0.1 T. The temperature dependence of magnetic susceptibility χ for NaVGe₂O₆ is shown in Fig.2. This dependence shows a broad maximum at T_M characteristic

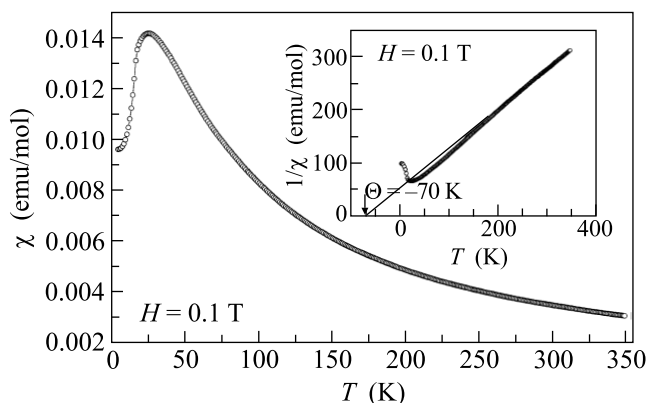


Fig.2. The temperature dependence of magnetic susceptibility χ of NaVGe₂O₆. The inset shows inverse susceptibility $1/\chi$. The straight line represents linear fit of high-temperature part by the Curie-Weiss law

of quasi-one-dimensional magnetic compounds. Below T_M , $\chi(T)$ has an inflection point at T_N which can be seen as a sharp peak in $\partial\chi/\partial T$. The weak upturn at the lowest temperatures is due likely to a small amount of magnetic impurities and deviations from stoichiometry.

The specific heat C in the range 6–300 K was measured in a “Termis” quasi-adiabatic calorimeter. The peak in the $C(T)$ curve is seen at the same temperature where the $\partial\chi/\partial T$ is maximum.

The temperature dependencies of $\chi(T)$ and $C(T)$ obtained on NaVGe₂O₆ are qualitatively similar to these measured on LiVGe₂O₆ [4, 7], but the temperatures of short range and long range magnetic ordering are sig-

nificantly lower in former compound. While the magnetic structure of NaVGe₂O₆ at low temperatures can be unambiguously determined only in neutron scattering measurements, the experimental data obtained strongly suggest that the ground state of this pyroxene is an antiferromagnetic one.

The Weiss temperature Θ and the effective magnetic moment μ_{eff} were determined from the $\chi(T)$ dependence at high temperature in accordance with a Curie-Weiss law

$$\chi = \mu_{\text{eff}}^2 N_A / 3k_B (T + \Theta), \quad (1)$$

where N_A is the Avogadro number, k_B is the Boltzmann constant.

The temperature of broad maximum T_M at $\chi(T)$ dependence is related to the value of exchange interaction J_{\parallel} within the chains [8]:

$$T_M = 1.282 J_{\parallel}. \quad (2)$$

The inflection point for $\chi(T)$ corresponds to the Neel temperature T_N . An analysis, as given in [9], of the values of Neel temperature T_N and the exchange interaction J_{\parallel} within the chains yields the value of exchange interaction between the chains:

$$J_{\perp} = T_N / 1.28n [\ln(5.8 J_{\parallel} / T_N)]^{1/2}, \quad (3)$$

where $n = 4$ is a number of nearest neighboring chains.

The parameters of the magnetic subsystem of NaVGe₂O₆ defined by Eqs. (1)–(3) are summarized in Table. The ratio of J_{\perp}/J_{\parallel} characterizes the “one-dimensionality” of the magnetic subsystem. As compared with LiVGe₂O₆ the low-dimensional character of new compound is less pronounced, i.e. the ratio of J_{\perp}/J_{\parallel} in NaVGe₂O₆ is twice that in LiVGe₂O₆ and also the temperatures of short range T_M and long range T_N magnetic ordering are much closer to each other in NaVGe₂O₆ than in LiVGe₂O₆.

The $C(T)$ dependencies at low temperatures are well fitted by a cubic term βT^3 . However, the value of β can not be used for determination of the Debye temperature since both the phonon and magnetic subsystems

of antiferromagnet give cubic terms in the specific heat at low temperatures. Moreover, the magnetic contribution to the specific heat in low-dimensional magnetic systems is smeared over a wide temperature range, at least up to double T_M . The low values of T_N and T_M in NaVGe_2O_6 allow however the fitting of the experimental data at high temperatures by the Einstein model. This fitting in the range 50–280 K was done using three

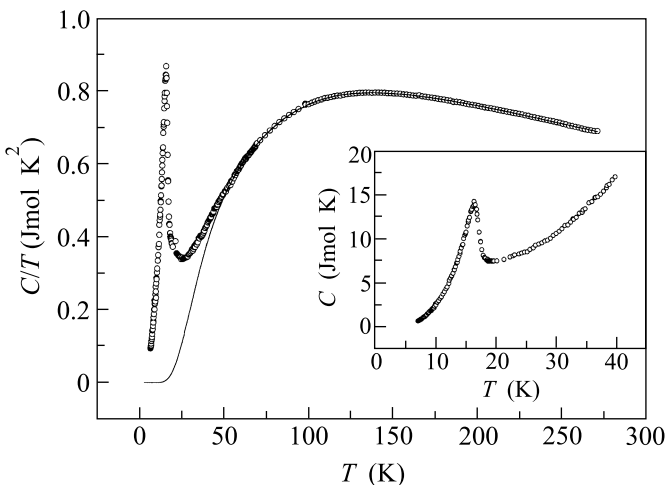


Fig.3. The temperature dependence of normalized specific heat C/T of NaVGe_2O_6 . The solid line represents the fit by three Einstein modes. The inset shows $C(T)$ dependence at low temperatures

Einstein modes, as given in Table. The extrapolation of the calculated curve to low temperatures allows for the subtraction of the lattice contribution. The experimental C/T vs. T curve as well as the curve obtained from the fitting procedure are shown in Fig.3. The area between experimental and calculated curves determines the magnetic entropy ΔS_{magn} released on the ordering

of the magnetic subsystem. The experimental value of $\Delta S_{\text{magn}} = 9 \text{ J/mol} \cdot \text{K}$ is slightly less than the theoretical estimate $\Delta S_{\text{magn}} = R \ln(2S + 1) = 9.13 \text{ J/mol} \cdot \text{K}$. Less than half of magnetic entropy ΔS_{AF} in NaVGe_2O_6 is released below the Neel temperature, which is typical for low-dimensional magnetic systems.

In summary, a study of structural, thermal and magnetic properties of a new low-dimensional metaloxide compound NaVGe_2O_6 with the pyroxene structure was performed. On substitution of Na for Li in this structure the quasi-one-dimensional character of the pyroxene magnetic subsystem became less pronounced. The exchange interaction parameter within the chains J_{\parallel} decreases while the value of interchain exchange interactions J_{\perp} does not change significantly. A long-range three-dimensional antiferromagnetic order is established in NaVGe_2O_6 at low temperatures.

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