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Long range Néel order in the quasi-one-dimensional vanadium-based $(S=1)$ pyroxenes $(\mathrm{Li,Na})\mathrm{V}(\mathrm{Si,Ge})_2\mathrm{O}_6$

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The long range Néel order formation in quasi-one-dimensional vanadium-based $(S=1)$ chain compounds with pyroxenes structure $(\mathrm{Li,Na})\mathrm{V}(\mathrm{Si,Ge})_2\mathrm{O}_6$ has been established at low temperatures. The main parameters of the magnetic subsystem of these compounds were estimated through the measurement of specific heat and magnetic susceptibility. The temperature distribution of magnetic entropy released at short range and long range magnetic ordering was found through comparison with isostructural nonmagnetic Sc-based pyroxenes $(\mathrm{Li,Na})\mathrm{Sc}(\mathrm{Si,Ge})_2\mathrm{O}_6$. At substitution of Na for Li and Ge for Si, the systematic enlargement of intrachain exchange interaction parameter $\mathbf{J}_{\parallel}$ as compared to interchain exchange interaction parameter $\mathbf{J}_{\perp}$ results in increasing "one dimensionality" in this family of complex metaloxides.

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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 lowest excited states are separated by a finite energy gap from a ground state.[1] This is in contrast with the case of half-integer spin chains where the magnetic excitation spectrum is gapless.[2] The gap can be introduced into the magnetic excitation spectrum of half-integer spin chain through the dimerization of the uniform chain. This dimerization known as spin-Peierls transition can occur due to magnetoelastic coupling in an intrinsically unstable quantum spin chain. In case of spin-Peierls transition, the opening of a spin gap is manifested by sharp isotropic decrease of magnetic susceptibility accompanied by the lattice distortions.[3] As of now, very few compounds possessing the spin-Peierls ground state have been found, mainly because of the "negative" role of interchain interactions at low temperatures. These interactions efficiently transform the quasi-one-dimensional systems into three-dimensional ones, resulting in a formation of antiferromagnetic or ferromagnetic ground states.[4,5]

It was conjectured that $\mathrm{LiVGe_2O_6}$ pyroxene represents a remarkable example of a compound that combines the properties of both integer and half-integer quantum spin chains.[6] The idea was that an anomalously large biquadratic exchange interaction closes the Haldane gap in $S=1$ spin chain and this now gapless integer spin chain undergoes a spin-Peierls phase transition at 22 K. The essence of microscopic mechanism leading to predominance of biquadratic exchange is the compensation of primarily antiferromagnetic bilinear exchange through two singly occupied lowest orbitals by virtual ferromagnetic bilinear exchange through the third orbital with slightly higher energy.[7] The thermodynamics of bilinear–biquadratic $S=1$ spin chain was discussed in Ref. 8, where it was found that the biquadratic exchange in $\mathrm{LiVGe_2O_6}$ is ferromagnetic. The spin-singlet ground state was postulated for this compound based on analysis of magnetic susceptibility data. The disturbing feature of this analysis was the presence of weak midgap susceptibility anomaly, which was finally attributed to nonmagnetic impurities.[9]

The subsequent experimental studies did not confirm however the gapped ground state of $\mathrm{LiVGe_2O_6}$. From Li^7 nuclear magnetic resonance studies[10,11] it was concluded that the ground state of this compound is antiferromagnetic with unusually big gap in the spectrum of spin excitation. The neutron and x-ray diffraction measurements indicated the low-temperature Néel state driven by ferromagnetic interchain coupling; no structural distortions associated with this transition were observed.[12]

Despite the fact that the Néel ground state was unambiguously established for $\mathrm{LiVGe_2O_6}$ at low temperatures it was of interest to define the nature of other vanadium-based pyroxenes. Taking into account the sensitivity of spin-chain compounds to parameters of intrachain and interchain interactions it is impossible to predict beforehand their ground states on the basis of structural considerations only. In the present work, the systematic study of the physical properties of quasi-one-dimensional vanadium-based metaloxide compounds $(\mathrm{Li,Na})\mathrm{V}(\mathrm{Si,Ge})_2\mathrm{O}_6$ was performed and the formation of Néel ground state in every member of this family of compounds was established.

The crystal structures of $(\mathrm{Li,Na})\mathrm{VSi_2O_6}$ pyroxenes are monoclinic with a space group C2/c.[13] That of $\mathrm{LiVGe_2O_6}$ is monoclinic with a space group $\mathrm{P2_1/c}$,[6] that of $\mathrm{NaVGe_2O_6}$ is probably monoclinic with a space group C2/c. The structures of these compounds contain isolated chains of $\mathrm{VO_6}$ edge-sharing octahedra running along the *c* axis. These chains are separated by double chains of distorted $\mathrm{SiO_4}$ or $\mathrm{GeO_4}$ tetrahedra. In the crystal structure of pyroxenes the valence state of vanadium is 3+ and V ions have the integer spin $S=1$. The interchain interaction in pyroxenes is strongly suppressed due to the presence of double nonmagnetic chains of $\mathrm{SiO_4}$ or $\mathrm{GeO_4}$ tetrahedra.

The solid state synthesis of $(\mathrm{Li,Na})\mathrm{V}(\mathrm{Si,Ge})_2\mathrm{O}_6$ pyroxenes was carried out at 900 °C in an evacuated silica tube for several days from the stoichiometric mixture of $\mathrm{Li_3VO_4}(\mathrm{Na_2SiO_3},\mathrm{Na_4Ge_9O_{20}})$, $\mathrm{V_2O_3}$, and $\mathrm{SiO_2}(\mathrm{GeO_2})$. $\mathrm{Li_3VO_4}(\mathrm{Na_2SiO_3},\mathrm{Na_4Ge_9O_{20}})$ prepared by heating the mix-

TABLE I. The crystal structure parameters of $(\mathrm{Li,Na})\mathrm{V}(\mathrm{Si,Ge})_2\mathrm{O}_6$ pyroxenes.

Compound	a,A	b,A	c,A	β	θ,K
$\mathrm{LiVSi_2O_6}$	9.634(4)	8.586(2)	5.304(2)	109.69(3)	532
$\mathrm{LiVGe_2O_6}$	9.863(4)	8.763(2)	5.409(1)	108.24(1)	433
$\mathrm{LiVSi_2O_6}$	9.6339(4)	8.7413(2)	5.2960(3)	109.905(2)	482
$\mathrm{LiVGe_2O_6}$	9.62(5)	8.72(3)	5.28(8)	106.8(7)	392

ture of $\mathrm{Li_2CO_3(Na_2CO_3)}$ and $\mathrm{V_2O_5(SiO_2,GeO_2)}$ at 800 °C in air. Light yellow and light green products of synthesis were obtained. The purity and phase compositions of the samples were checked by powder x-ray diffraction at room temperature. Single phase and correspondence of crystal structure to those of pyroxenes were confirmed. The parameters of crystal structure of $(\mathrm{Li,Na})\mathrm{V}(\mathrm{Si,Ge})_2\mathrm{O}_6$ at room temperature are brought together in Table I.

The solid state synthesis of $(\mathrm{Li,Na})\mathrm{Sc}(\mathrm{Si,Ge})_2\mathrm{O}_6$ pyroxenes was carried out at 1000 °C in air from the stoichiometric mixture of $\mathrm{Li_2CO_3(Na_2CO_3)}$, $\mathrm{Sc_2O_3}$ and $\mathrm{SiO_2(GeO_2)}$. These nonmagnetic compounds were used to isolate magnetic contribution in the specific heat of $(\mathrm{Li,Na})\mathrm{V}(\mathrm{Si,Ge})_2\mathrm{O}_6$ pyroxenes. The magnetic susceptibility χ in the range 2–350 K was measured by a "Quantum Design" SQUID-magnetometer. The specific heat C in the range 5–300 K was measured by a "Termis" quasiadiabatic microcalorimeter.

The temperature dependences of magnetic susceptibility χ of $(\mathrm{Li,Na})\mathrm{V}(\mathrm{Si,Ge})_2\mathrm{O}_6$ pellet samples are shown in Fig. 1. For every pyroxene studied the $\chi(T)$ dependence shows a broad maximum at T_M characteristic for quasi-one-dimensional magnetic compounds. This maximum indicates the formation of a regime of short-range correlations within the chains. At $T<T_M$ the $\chi(T)$ dependences bend at certain temperatures T_N which can be seen as sharp peaks in $d\chi/dT$ dependences. The weak up turns in χ at lowest temperatures are due to a small amount of magnetic impurities and deviations from stoichiometry. Some important parameters of $(\mathrm{Li,Na})\mathrm{V}(\mathrm{Si,Ge})_2\mathrm{O}_6$ magnetic subsystems can be estimated from these data as follows.

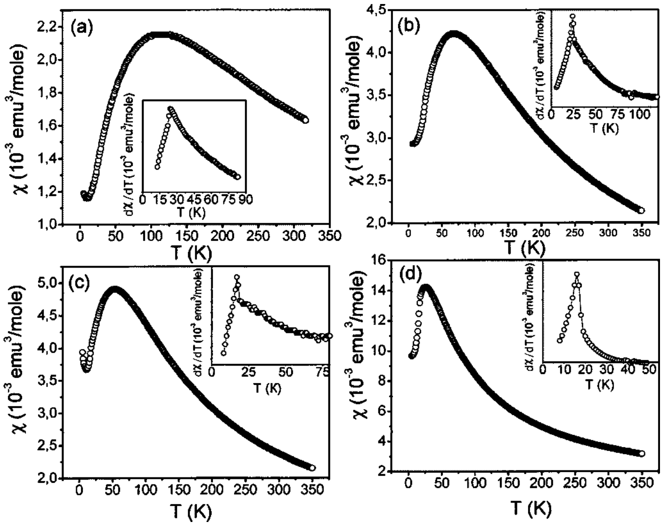

FIG. 1. The temperature dependences of magnetic susceptibility of $\mathrm{LiVSi_2O_6}$ (a), $\mathrm{LiVGe_2O_6}$ (b), $\mathrm{NaVSi_2O_6}$ (c), $\mathrm{NaVGe_2O_6}$ (d).

The Weiss temperatures Θ and effective magnetic moments μ_{eff} can be derived from the slopes of inverse magnetic susceptibility curves at high temperatures in accordance with a Curie–Weiss law

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

where N_A is the Avogadro number, k_B is the Boltzmann constant. In every member of the $(\mathrm{Li,Na})\mathrm{V}(\mathrm{Si,Ge})_2\mathrm{O}_6$ family the effective magnetic moment μ_{eff} roughly corresponds to the spin-only part of magnetization, indicating, the freezing of orbital motion. The Weiss temperatures Θ are negative in every case pointing to a predominance of antiferromagnetic exchange interaction within the chains.

The temperature of the broad maximum T_M at $\chi(T)$ dependence is related to the value of the intrachain exchange interaction parameter $J_\parallel$,[14]

$$T_M = 1.35 J_\parallel. \tag{2}$$

The bend at $\chi(T)$ dependence at $T<T_M$ corresponds to the Néel temperature T_N. On the basis of the analysis given in Ref. 15, the values of Néel temperature T_N and exchange interaction $J_\parallel$ within the chains allow to determine the value of exchange interaction between the chains,

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

where n is a number of nearest neighboring chains (in the present case $n=4$).

The ratio of $J_\perp/J_\parallel$ characterizes "one dimensionality" of the magnetic subsystem. The parameters of $(\mathrm{Li,Na})\mathrm{V}(\mathrm{Si,Ge})_2\mathrm{O}_6$ defined by Eqs. (1)–(3) are systemized in Table II. The data presented in Table II evidence the trends in magnetic subsystem parameters at chemical substitutions in this family of compounds. Namely, at substitution of Na for Li and Ge for Si the values of exchange interactions within the chains $J_\parallel$ increase while the values of interchain exchange interactions $J_\perp$ do not vary significantly. The latter circumstance predetermines the closeness of Néel temperatures T_N in every member of the $(\mathrm{Li,Na})\mathrm{V}(\mathrm{Si,Ge})_2\mathrm{O}_6$ pyroxenes family. Most clearly the quasi-one-dimensional character of pyroxenes magnetic structure is seen in $\mathrm{LiVSi_2O_6}$ [Fig. 1(a)] where the difference in T_M and T_N is of maximum. This is also in accordance with the minimal value of ratio $J_\perp/J_\parallel$ in this compound. On the contrary, the T_M and T_N are rather close in $\mathrm{NaVGe_2O_6}$, which is in correspondence with the larger value of $J_\perp/J_\parallel$. It is worth noting, that Eq. (3) for interchain exchange interactions $J_\perp$ does not take into ac-

TABLE II. The magnetic subsystem parameters of (Li,Na)V(Si,Ge)$_2$O$_6$ pyroxenes.

Compound	Θ,K	T_M,K	T_N,K	$J_\parallel$,K	$J_\perp$,K	$J_\perp/J_\parallel$	$\Delta S_{T<TN}/S$
LiVSi$_2$O$_6$	−290	110	21.6	82	2.4	0.029	0.10
LiVGe$_2$O$_6$	−130	60	24	44	3.0	0.068	0.18
LiVSi$_2$O$_6$	−78	48	17.4	36	2.2	0.061	0.19
LiVGe$_2$O$_6$	−33	22	16.4	16	2.4	0.15	0.40

count the effects of magnetocrystalline anisotropy. In the presence of strong anisotropy, the expression for $J_\perp$ would need to be modified. This information is unavailable from the measurements on the powder samples, however.

The temperature dependences of specific heat in (Li,Na)V(Si,Ge)$_2$O$_6$ are shown in Fig. 2. The well-pronounced peaks in $C(T)$ curves are seen at the same temperatures where the $d\chi/dT$ curves are at maximums. Note, that in LiVSi$_2$O$_6$ an additional anomaly is seen at 204 K. It corresponds probably to some structural change in this compound, but its origin has not been clarified yet. The $C(T)$ dependences at the lowest temperatures are well fitted by a cubic term βT^3. However, the values of β cannot be used directly for Debye temperature estimations since both phonon and magnon subsystems of antiferromagnet give cubic terms into total specific heat at low temperatures. In order to get these values, the separation of magnetic and lattice contributions to the specific heat C should be performed. An obvious method is to apply a corresponding states analysis,[16] using the specific heat of a diamagnetic isostructural compound for reference.

To separate magnetic contribution in specific heat of vanadium-based pyroxenes the temperature dependences of specific heat of Sc-based nonmagnetic pyroxenes were used. In essence, the procedure of corresponding states analysis assumes that the lattice entropy gain S of isomorphous compounds may be expressed by a common function ϕ, whose argument is the reduced temperature T/Θ.[17] For two compounds, at corresponding temperatures T_1 and T_2, it follows that if $S_1=S_2$, then $\phi(T_1/\Theta_1)=\phi(T_2/\Theta_2)$ and therefore $T_1/\Theta_1=T_2/\Theta_2$, or $T_1/T_2=\Theta_1/\Theta_2$. This latter ratio is denoted as corresponding states ratio r. If the corresponding states assumption is valid, r must be a constant. In practice, r generally is not constant but rather has a slight temperature dependence. If there is a magnetic contribution to the total measured entropy for one of the compounds being compared, this contribution must be substracted from that entropy before the corresponding states argument may be applied and the resulting entropy used to obtain the value of r. Since that contribution is generally unknown and changing with temperature, the total expected magnetic entropy contribution must be subtracted instead. As this will be an overestimate throughout the region where there is a magnetic contribution to the entropy the value of r will exhibit the near constant behavior $r=a+bT$ only at high temperatures. The lattice contribution to the heat capacity of the vanadium-based pyroxenes C_{lat} may then be obtained from heat capacity C_{Sc} of Sc-based pyroxenes as

$$\begin{aligned} C_{\text{lat}}(T) &= T\,\mathrm{d}S_{\text{lat}}(T)/\mathrm{d}T = T[\mathrm{d}S_{\text{Sc}}(rT)/\mathrm{d}(rT)] \times \mathrm{d}(rT)/\mathrm{d}T \\ &= C_{\text{Sc}}(rT)(a+2bT)/(a+bT). \end{aligned} \tag{4}$$

The $C(T)$ dependences in (Li,Na)Sc(Si,Ge)$_2$O$_6$ are shown in Fig. 3. These curves show no anomalous behavior whatsoever, indicating the absence of structural changes in the temperature range studied. The temperature dependences of magnetic entropy in (Li,Na)V(Si,Ge)$_2$O$_6$, obtained through the procedure of corresponding states analysis, are

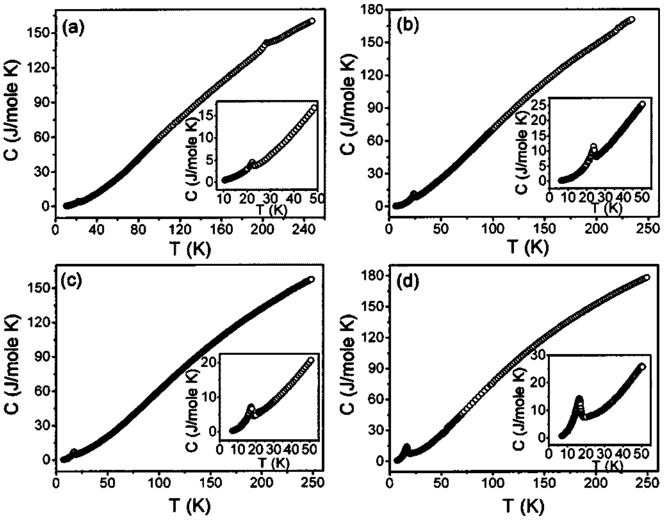

FIG. 2. The temperature dependences of specific heat of LiVSi$_2$O$_6$ (a), LiVGe$_2$O$_6$ (b), NaVSi$_2$O$_6$ (c), NaVGe$_2$O$_6$ (d).

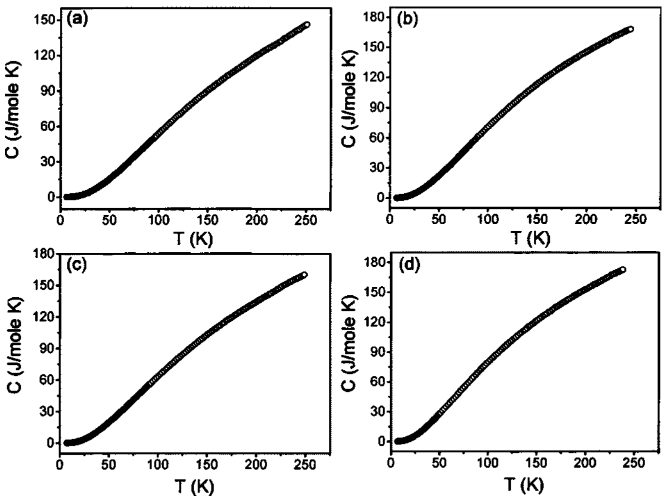

FIG. 3. The temperature dependences of specific heat of LiScSi$_2$O$_6$ (a), LiScGe$_2$O$_6$ (b), NaScSi$_2$O$_6$ (c), NaScGe$_2$O$_6$ (d).

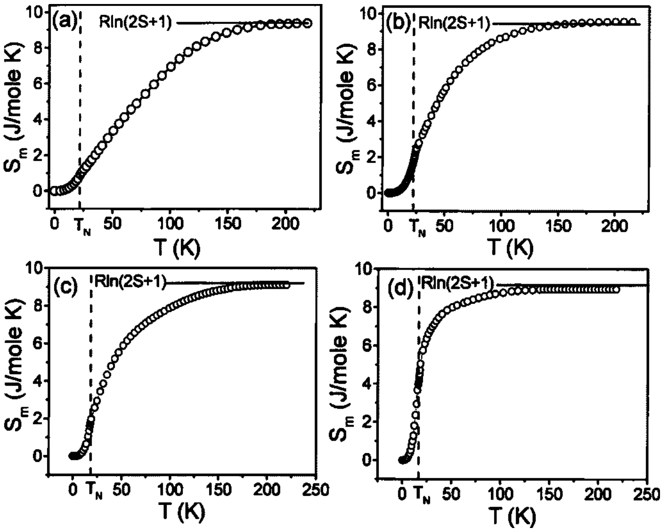

FIG. 4. The temperature dependences of magnetic entropy of $LiVSi_2O_6$ (a), $LiVGe_2O_6$ (b), $NaVSi_2O_6$ (c), $NaVGe_2O_6$ (d).

shown in Fig. 4. Evidently, the large part of magnetic entropy is released well above the Néel temperatures, which again is the signature of the low-dimensional magnetic system. The ratios of magnetic entropies released below Néel temperatures to total magnetic entropy $R\ln(2s+1) = 9.13$ J/mol K released over the entire temperature range are given in Table II. The subtraction of magnetic specific heat from total specific heat allows estimation of Debye temperatures θ in $(Li,Na)V(Si,Ge)_2O_6$. These estimates are presented in Table I.

In summary, the systematic study of the structural, thermal, and magnetic properties of new low-dimensional metaloxide compounds with pyroxene structure $(Li,Na)V(Si,Ge)_2O_6$ was performed. Based on similarity in behavior of each member of the vanadium-based pyroxenes family it can be concluded that long-range three-dimensional Néel order is established at low temperatures analogous to that in $LiVGe_2O_6$. At substitution of Na for Li and Ge for Si the quasi-one-dimensional character of the pyroxenes magnetic subsystem became more pronounced. The main parameters of crystal structure and magnetic exchange interactions in $(Li,Na)V(Si,Ge)_2O_6$ are determined. The data presented in Tables I and II indicate that the crystal lattice parameters of vanadium-based pyroxenes are not strongly influenced by chemical substitutions in this family of compounds. However, the parameters of magnetic exchange vary significantly. It means that appreciable variations in magnetic properties are obtained through a slight change in parameters of the magnetic exchange interactions.

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