Specific Heat of $Na_{1-x}V_2O_5$ Single Crystals

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Temperature dependences of the specific heat C and the magnetic susceptibility χ of $Na_{1-x}V_2O_5$ single crystals ($x = 0$, 0.01, 0.02, 0.03, and 0.04) are studied. In NaV_2O_5, the transition to the spin-gap state ($T_c = 34$ K) is accompanied by a sharp decrease in χ while C exhibits a λ-shaped anomaly. At low temperatures, the specific heat of NaV_2O_5 is approximated by the sum of phonon $\sim T^3$ and magnon $\sim \exp(-\Delta/T)$ contributions, which makes it possible to estimate the Debye temperature $\Theta_D = 336$ K and the gap in the magnetic excitation spectrum $\Delta = 112$ K. With the departure from stoichiometry, the anomalies observed in the behavior of χ and C are spread and shifted to lower temperatures. The low-temperature specific heat of nonstoichiometric samples is determined by the sum of phonon and magnon components and the contribution due to the presence of defects. The values of magnetic entropy characterizing the phase transitions in $Na_{1-x}V_2O_5$ are calculated. © 2001 MAIK "Nauka/Interperiodica".

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The characteristic features of the ground-state formation in NaV_2O_5 have much been investigated since the discovery of the phase transition in this compound at $T_c \sim 34$ K [1]. According to the existing concepts, the charge transfer at this temperature occurs between V sites in NaV_2O_5, resulting in structural distortions and the appearance of an energy gap in the magnetic excitation spectrum [2, 3]. The crystal structure of NaV_2O_5 is formed by corrugated layers of VO_5 complexes separated from each other by Na atoms. At high temperatures, all V sites are equivalent and the formal valence of V is +4.5 [4]. This means that a single $3d$ electron that is not involved in the ionic-covalent bonds is divided between two nearest V ions and occupies the bonding V–O–V molecular orbital [5]. These orbitals form rungs of spin ladders shifted relative to each other by a half-period along the b axis in the ab plane.

At low temperatures, the NaV_2O_5 structure has two inequivalent V sites with formal valences $4.5 - \delta$ and $4.5 + \delta$, where δ determines the deviation of the valence from its mean value (below, we will use the notations V^{4+} and V^{5+} for these ions). The magnetic V^{4+} and nonmagnetic V^{5+} ions are positioned in the spin ladders in a zigzag manner. According to [6], the alternation of the exchange interaction in these ladders gives rise to an energy gap in the magnetic excitation spectrum of NaV_2O_5.

The specific heat of NaV_2O_5 single crystals, including those with Na deficiency, was considered in a number of papers [7–12]. Although the data reported in these publications testify to the sensitivity of the specific heat to the chemical composition, the effect of deviation from stoichiometry on the specific heat of $Na_{1-x}V_2O_5$ has never been thoroughly investigated over a wide temperature range.

This paper describes the study of $Na_{1-x}V_2O_5$ single crystals ($x = 0$, 0.01, 0.02, 0.03, and 0.04) grown from the melt by using $NaVO_3$ as a flux. The samples had the shape of parallelepipeds with characteristic dimensions of several millimeters and characteristic mass of several ten milligrams. The magnetic susceptibility was measured by a Quantum Design SQUID magnetometer in a magnetic field of 0.1 T in the temperature interval 5–80 K. The specific heat of single crystals was measured by an adiabatic microcalorimeter in the temperature interval 5–160 K.

The temperature dependences of the magnetic susceptibility of $Na_{1-x}V_2O_5$ are presented in Fig. 1. These dependences show that, with the deviation from the stoichiometry, the anomaly accompanying the phase transition becomes less pronounced and shifts to lower temperatures. Simultaneously, the contribution made by Na vacancies to χ noticeably increases. The appearance of the vacancies gives rise to the transition of part
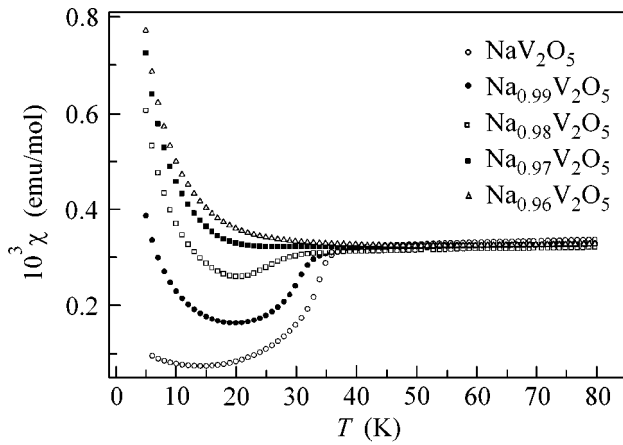
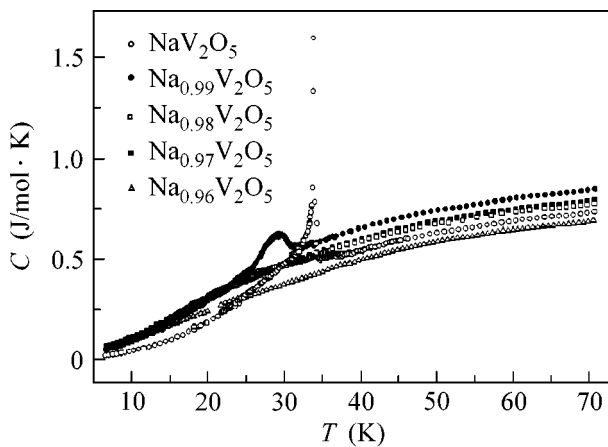**Fig. 1.** Temperature dependences of the magnetic susceptibility of $Na_{1-x}V_2O_5$ single crystals.

Fig. 2. Temperature dependences of the specific heat of $Na_{1-x}V_2O_5$ single crystals.

The temperature dependences of the specific heat of $Na_{1-x}V_2O_5$ are presented in Fig. 2. The anomaly accompanying the phase transition is most pronounced in the sample with the stoichiometric composition. Outside the phase transition region, the specific heat of this crystal takes the lowest values, as compared to the other samples. At temperatures $T < T_c$, the specific heat increases with x (except for the sample with $x = 0.04$). The temperatures at which the anomalies of specific heat and kinks in the temperature dependences of magnetic susceptibility are observed allow one to determine the dependence of the phase transition temperature on the composition for $Na_{1-x}V_2O_5$ compounds. These data correlate well with each other and show that, with the departure from the stoichiometry, the transition temperature varies according to the law $dT_c/dx = -4$ K per 1% Na deficiency.

The analysis of the temperature dependences of specific heat was performed on the assumption that the specific heat is described by the sum of phonon and magnon components plus the contribution due to the presence of Na vacancies in the samples with a nonstoichiometric composition.

In the temperature range 5–20 K, the energy gap Δ that occurs in the magnetic excitation spectrum of a stoichiometric sample can be considered as temperature independent. Then, the temperature dependence of the specific heat can be approximated by the sum of the phonon $C_{ph} = \beta T^3$ and magnon $C_{mag} = A_0 \exp(-\Delta/T)$ components. The coefficient of the phonon component $\beta = 12\pi^4 R\nu/5\Theta_D^3$, where R is the universal gas constant and $\nu = 8$ is the number of atoms in the formula unit, allows one to estimate the Debye temperature: $\Theta_D \sim$ 336 K. According to the data obtained from other measurements, this value falls within 280–435 K [13–15]. The value of energy gap estimated on the basis of the experimental data, $\Delta = (112 \pm 18)$ K, agrees well with the value obtained for the gap in the magnetic excitation spectrum from the neutron diffraction studies ($\Delta = 114$ K) [3]. The approximation of the experimental data for the nonstoichiometric $Na_{1-x}V_2O_5$ samples by the sum of phonon and magnon contributions yields grossly underestimated values for the energy gap.

To take into account the additional contribution that is made by Na vacancies to the specific heat, it is necessary to introduce an additional term: $C_x = B_x(T/\Delta_0)^n$. The phonon contribution to the specific heat of nonstoichiometric samples, $C_{ph} = \beta T^3$ with $\beta = 0.425$ mJ/mol K^4, is assumed to be equal to that in the stoichiometric sample. On the coefficients of the magnon (A_x) and vacancy (B_x) components, the following conditions were imposed: $A_x = A_0(1 - x/x_C)$ and $B_x = B_4 x/x_C$. The coefficients A_x and B_x, the energy gap $\Delta(x)$, and the exponent $n(x)$ that correspond to the closest agreement between
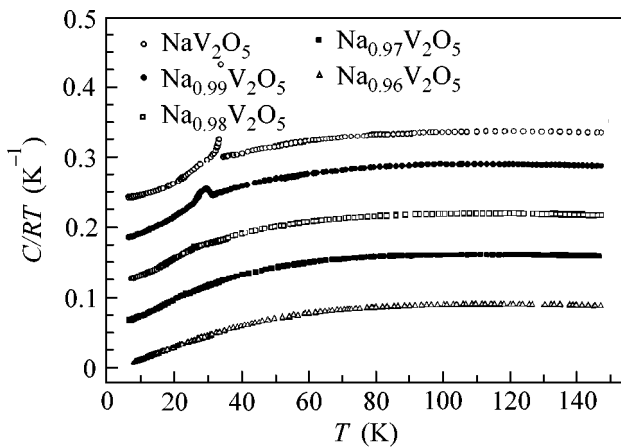
of the V^{4+} ions to the V^{5+} ionization state, and the remaining noncompensated moments of V^{4+} make an additional contribution to the susceptibility. In $Na_{1-x}V_2O_5$ samples with $x = 0.03$ and 0.04, no decrease in the magnetic susceptibility was observed at low temperatures. This result is in good agreement with the estimated value of critical defect concentration $x_c = 0.035$ above which the gap in the magnetic excitation spectrum of $Na_{1-x}V_2O_5$ does not appear. The estimate for critical defect concentration follows from the Nagaoka theorem [13], which gives $x_c \sim \Delta/2t_\parallel$. Here, $\Delta \sim 100$ K is the gap in the magnetic excitation spectrum of NaV_2O_5 and $t_\parallel \sim 1400$ K is the kinetic energy of an electron moving along the spin ladder [14]. It should be noted that the estimate obtained using the Nagaoka theorem in this case not only is correct within an order of magnitude but also quantitatively agrees with the experimental results.

Fig. 3. Temperature dependences of the reduced specific heat C/RT of $Na_{1-x}V_2O_5$ single crystals. For convenience, the curves are spaced at 0.0625 K^{-1} intervals.

Fig. 4. Magnetic component of the specific heat of $Na_{1-x}V_2O_5$ single crystals.

the theory and the experimental data on the specific heat of $Na_{1-x}V_2O_5$ are presented in the table. One can see that, as x increases, the energy gap in $Na_{1-x}V_2O_5$ decreases and the exponent in the vacancy term converges to two. The appearance of the term quadratic in temperature in the specific heat of nonstoichiometric samples at low temperatures could be attributed to the magnons in a two-dimensional antiferromagnet. However, it should be noted that the formation of a long-range magnetic ordering with increasing concentration of Na vacancies was never observed in $Na_{1-x}V_2O_5$.

Figure 3 shows the temperature dependences of C/T in the interval 5–150 K. The determination of the entropy of phase transition in $Na_{1-x}V_2O_5$ presents considerable problems, because the fluctuation region in this low-dimensional compound extends to high temperatures [15]. To set off the magnon contribution to the specific heat, the phonon contribution outside the fluctuation region in the dependence of C/T on T was approximated by a polynomial. Subtracting the phonon contribution from the experimental dependences, one can obtain the magnetic component of the specific heat, as shown in Fig. 4. The areas under these curves determine the magnetic entropy released upon the phase transition. The values of ΔS_{mag} determined in this way for $Na_{1-x}V_2O_5$ are shown in the table. These values should be compared with the theoretical estimate $\Delta S_{mag} = R\ln(2S + 1) = 5.76$ J/mol K, which is valid for an ordered magnetic system with spin $S = 1/2$. For the stoichiometric sample, a good agreement with the theoretical estimate can be achieved upon the introduction of upper bound $T \sim 65$ K to the region of calculations, which approximately corresponds to the transition from the regime of quasi-one-dimensional magnetic fluctuations to the regime of quasi-three-dimensional ones [15]. In the samples with the composition close to
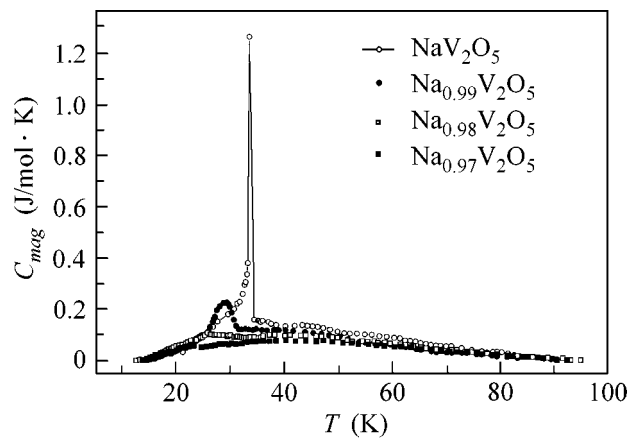
the stoichiometric one, the magnetic component of the specific heat has a peak at the phase transition point and a diffuse fluctuation region. As the deviation from the stoichiometry increases, the magnetic entropy released at the phase transition decreases and the peak becomes indistinguishable.

Thus, a systematic study of the magnetic susceptibility and the specific heat of $Na_{1-x}V_2O_5$ ($x = 0$, 0.01, 0.02, 0.03, and 0.04) showed that the phase transition is rapidly suppressed with the departure from the stoichiometry. A decrease in the phase transition temperature is accompanied by a decrease in the energy gap in the magnetic excitation spectrum; in the samples with $x > 0.03$, the gap is not observed. The appearance of the component $\sim T^2$ in the specific heat of nonstoichiometric samples at low temperatures can presumably be due to the hopping degree of freedom of the unpaired electrons on the bonding V–O–V molecular orbitals.

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