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Sequence of Phase Transitions in a Quasi-One-Dimensional β-$Na_{0.33}V_2O_5$ Compound with Variable Valence

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The thermal properties—specific heat, thermal conductivity, and thermal expansion coefficients—of a single crystal of quasi-one-dimensional variable-valence β-$Na_{0.33}V_2O_5$ compound were studied. With lowering temperature, it sequentially undergoes the structural (T_S ~ 230 K), charge (T_C ~ 136 K), and magnetic (T_N ~ 22 K) phase transitions. The structural transition at T_S, resulting in the ordering of the Na ions, and the charge ordering at T_C, resulting in the charge redistribution over the positions of V ions, are accompanied by the anomalies in the temperature dependences of all the studied properties. The magnetic ordering at T_N results in the appearance of the canted antiferromagnetic structure and manifests itself only in the anomaly in the temperature dependences of the thermal expansion coefficients. © *2004 MAIK "Nauka/Interperiodica".*

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Compounds relating to the family of vanadium bronzes of the β(β') type with general formula β(β')–$A_xV_2O_5$ (A = Na, Sr, Cu, etc.) are quasi-one-dimensional conductors [1]. The variable-valence sodium-based β-$Na_{0.33}V_2O_5$ compound belongs to this family. With lowering temperature, it undergoes the structural (T_S ~ 230 K), charge (T_C ~ 136 K), and magnetic (T_N ~ 22 K) phase transitions [2]. Under the hydrostatic pressure P ~ 8 GPa, the charge-ordered phase of β-$Na_{0.33}V_2O_5$ collapses and it undergoes the transition to the superconducting state at T_{SC} = 8 K [3]. The monoclinic crystal structure of this compound (Fig. 1) is typical of all vanadium bronzes in the β(β') phase and contains tunnels formed by the VO_6 and VO_5 complexes along the *b* axis. The Na ions are located inside the tunnels. At high temperatures, the vanadium ions in β-$Na_{0.33}V_2O_5$ occupy three crystallographically different positions: V1 in the octahedral oxygen environment forms zig-zag chains of edge-shared VO_6 octahedra along the *b* axis, V2 in the same environment forms double chains of angle-shared octahedra, and V3 forms zig-zag chains of edge-shared VO_5 pyramids [2]. The Na ions (*A*) also occupy two different crystallographic positions in the unit cell. With lowering temperature, the Na ions become structurally ordered at T_S and a superstructure of the 1 × 2 × 1 type arises along the *b* axis.

β-$Na_{0.33}V_2O_5$ is a compound with variable valence, because its unit cell contains one V^{4+} ion and five V^{5+} ions. At $T > T_C$, all vanadium sites are equivalent and β-$Na_{0.33}V_2O_5$ is a conductor. With lowering temperature, this compound undergoes at T_C the metal–insulator transition of the charge-ordering type; nonmagnetic V^{+5} ions occupy the V3 positions, while the V1 and V2 positions can be occupied by both V^{5+} and V^{4+}. According to [4], the magnetically active V^{4+} ions are at the V1 positions. Optical studies of β-$Na_{0.33}V_2O_5$ showed that the charge redistribution in the lattice is accompanied by strong polaron effects [5].

Although the magnetic subsystem in $Na_{0.33}V_2O_5$ is highly diluted, the canted antiferromagnetic structure is formed in this material at T_N [6]. The very fact that the

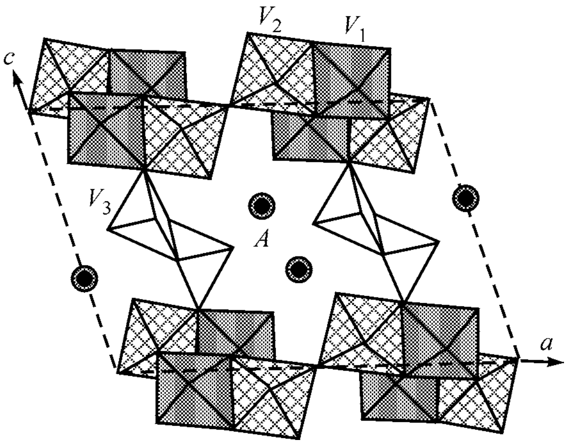

Fig. 1. Crystal structure of β-$Na_{0.33}V_2O_5$.

long-range magnetic order appears in a diluted structure indicates that, upon the charge ordering, the magnetically active V^{4+} ions are arranged in such a way as to provide for a rather strong exchange interaction between them.

To gain additional information on the kinetic and thermodynamic properties of this compound, the thermal capacity, thermal conductivity, resistivity, and thermal expansion coefficients of a β-$Na_{0.33}V_2O_5$ single crystal were measured in this work over a broad temperature range. Single crystals were grown from a melt using $NaVO_3$ as flux. The samples were parallelepipeds with characteristic sizes of 0.5 × 5 × 0.5 mm and with the largest size oriented along the *b* axis. The temperature dependences of the thermal capacity and resistivity were studied using a quasi-adiabatic microcalorimeter and an automated setup (Termis) for measuring resistivity. The thermal conductivity and the thermal expansion coefficients were studied by the methods of constant thermal flow and capacitive dilatometry, respectively.

The temperature dependence of the thermal capacity of β-$Na_{0.33}V_2O_5$ $C(T)$ in the range 5–300 K is shown in Fig. 2. A peak at the metal–insulator phase-transition temperature $T_C = 136$ K is clearly seen in this curve, and the slope of the $C(T)$ curve slightly changes after the temperature of structural phase transition at $T_S \sim 230$ K. The absence of anomaly in the thermal capacity at the magnetic ordering temperature $T_N \sim 22$ K can be explained in the following way. In the materials containing one-dimensional chains of exchange-coupled magnetic ions, the three-dimensional order in the whole magnetic subsystem appears due to the presence of a weak interchain interaction. This interaction and, hence, the ordering temperature are smaller than the intrachain interaction between the magnetic ions. Therefore, the magnetic entropy released at the three-dimensional ordering temperature is small and does not lead to the appearance of a noticeable anomaly in the thermal capacity. Moreover, the magnetic subsystem of β-$Na_{0.33}V_2O_5$ is highly diluted and its contribution to the thermal capacity is small on the background of the rapidly increasing phonon contribution.

The temperature dependence of the thermal capacity in the low-temperature range was approximated using two terms: $\beta T^3 + \gamma T^{3/2}$. The first term is responsible for the phonon contribution and the contribution from the magnetic subsystem of a three-dimensional antiferromagnet. The second term corresponds to the contribution from a three-dimensional ferromagnet, in accordance with the presence of a spontaneous magnetic moment below T_N. In this case, the estimate of the lower bound for the Debye temperature gives $\theta_D = 490$ K. A satisfactory approximation can also be obtained with only the first term βT^3. In this case, the numerical value of the parameter β gives a value of 456 K for the lower bound of the Debye temperature.

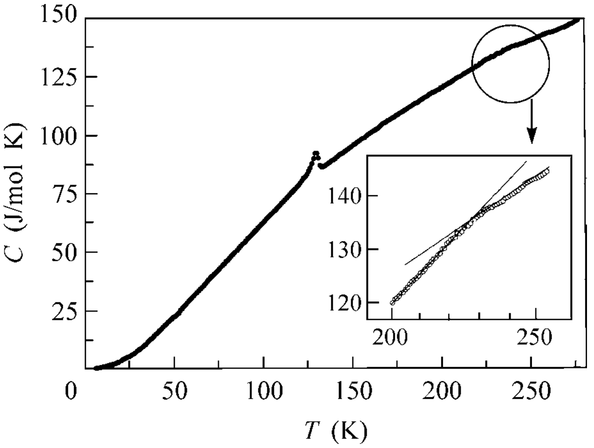

Fig. 2. Thermal capacity of β-$Na_{0.33}V_2O_5$.

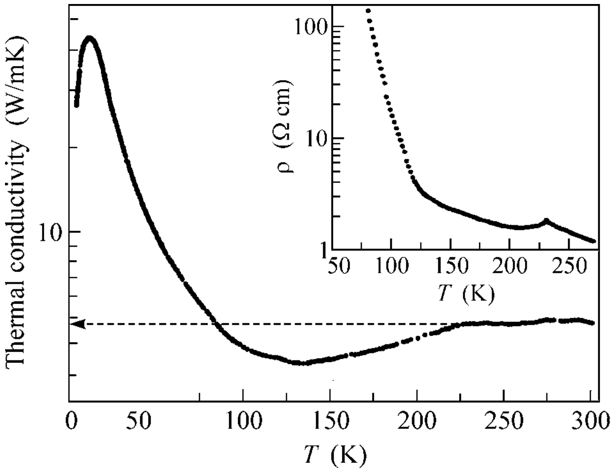

Fig. 3. Thermal conductivity of β-$Na_{0.33}V_2O_5$ along the *b* axis. The temperature dependence of the resistivity of β-$Na_{0.33}V_2O_5$ along the *b* axis is shown in the inset.

The temperature dependence of the thermal conductivity coefficient $\kappa(T)$ measured along the *b* axis of a β-$Na_{0.33}V_2O_5$ single crystal is presented in Fig. 3. With an increase in temperature, $\kappa(T)$ reaches its maximal value $\kappa_{max} \sim 45$ W/(m K) at $T \sim 13$ K. This maximum is characteristic of the phonon-assisted heat transfer and appears due to the increase in the number of phonons, on the one hand, and to a decrease in the phonon mean free path with lowering temperature, on the other. The metal–insulator transition at T_C is accompanied by a change in the sign of the $\kappa(T)$ slope in the interval T_C–T_S. The increase in the thermal conductivity of β-$Na_{0.33}V_2O_5$ at $T > T_C$ can be due to electron delocalization, i.e., to the electron redistribution over the vanadium sites. This process is likely terminated at the structural transition temperature T_S, above which the thermal conductivity is virtually independent of tem-

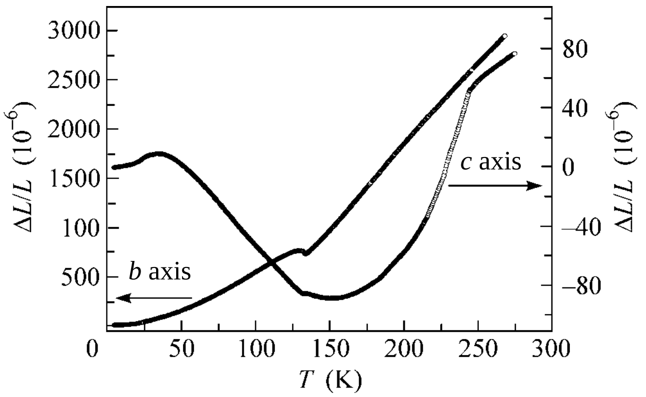

Fig. 4. The elongation per unit length along the *b* and *c* axes of β-$Na_{0.33}V_2O_5$.

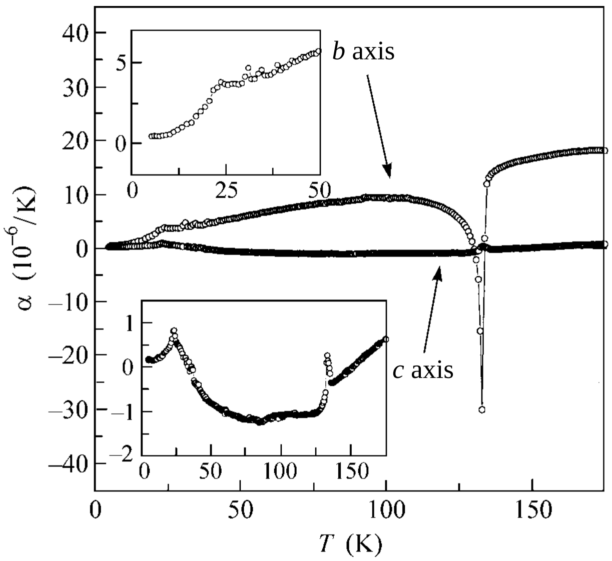

Fig. 5. Thermal expansion coefficients $\alpha_i(T)$ along the *b* and *c* axes of a β-$Na_{0.33}V_2O_5$ single crystal. The behavior of $\alpha_b(T)$ in the vicinity of T_N and $\alpha_c(T)$ over a broad temperature range are shown in the insets.

perature. The value $\kappa_0 \sim 5$ W/(m K) achieved by the thermal conductivity at $T > T_S$ corresponds, by the order of magnitude, to a "bad" metal.

The temperature dependence of the resistivity $\rho(T)$ of β-$Na_{0.33}V_2O_5$ measured along the *b* axis is shown in the inset in Fig. 3. The structural transition at T_S shows up in this curve as a break, and the metal–insulator transition at T_C is accompanied by a sharp increase in the resistivity.

The temperature dependences of the elongation per unit length along the crystallographic *b* and *c* axes of β-$Na_{0.33}V_2O_5$ are shown in Fig. 4. The thermal expansion in this crystal is highly anisotropic. With lowering temperature, the sample is strongly compressed along the *b* axis, while the size along the *c* axis slightly changes in the alternating manner. As the temperature lowers, the "invar" effect is observed along the *c* axis in the T_N–T_C interval: the sample length increases with cooling. This is likely due to the charge redistribution over the VI positions in the structure of β-$Na_{0.33}V_2O_5$. The thermal expansion coefficients α_i of the β-$Na_{0.33}V_2O_5$ single crystal are also highly anisotropic (Fig. 5). At $T < T_N$, they strongly change because of the spontaneous crystal striction in the magnetically ordered state.

The charge ordering at T_C is also accompanied by the anomalies in α_i, although they differ in magnitude and sign. A sharp anomaly is seen along the *b* axis, indicating that the single crystal is elongated jumpwise along this axis with lowering temperature. A charge-ordering peak observed for the *c* axis indicates that the single crystal is contracted along this direction. The anomaly in α_c is much smaller than in α_b, but both peak shapes suggest that the charge ordering has traits of the first-order phase transition. The fact that the charge and magnetic orderings are accompanied by the noticeable anomalies in the $\alpha_i(T)$ dependences points to the strong influence of the charge and magnetic subsystems on the lattice degrees of freedom in this compound.

We note in conclusion that the distribution of magnetically active V^{4+} ions over the crystallographic positions at low temperatures plays the decisive role in establishing the ground-state parameters of β-$Na_{0.33}V_2O_5$ and searching for the mechanisms responsible for the superconducting transition under pressure. This information can likely be obtained only from the resonance and neutron diffraction studies in conjunction with a certain model of the distribution of the V^{4+} and V^{5+} ions. The information obtained in this work and, in particular, the data on the thermal expansion anisotropy in β-$Na_{0.33}V_2O_5$ can be helpful in constructing such a model.

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