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Electrical Conductivity in Single-Crystals of Vanadium Oxide Bronzes

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Single-crystal electrical conductivity of vanadium oxide bronzes of the type $M_xV_2O_5$ (β-phase), where M = Li, Na, K has been studied from 300 to 900°K. These compounds are found to exhibit a reversible semiconductor–metal transition along [010] in the region of 340°K. The phase transition observed seems to be caused by vanishing of the activation energy of carrier mobility due to the shift of some vanadium atoms in the planes perpendicular to the B axis.

Introduction

Study of nonstoichiometric vanadium oxide bronzes (VOB) of the type $M_xV_2O_5$ is of considerable interest since these compounds may be used as model material for examining the mechanism of electron transport in transition-metal oxides. For this reason, conductivity measurements on these compounds have been repeatedly made (*1–4*). It has been definitely established that the charge transfer in VOB is realized via the auto-localized electrons (polarons). The carrier density remains constant over a wide range of temperature and is, in fact, equal to the number of alkali-metal atoms (*4*, *5*). Goodenough (*6*) has considered the problem of unpaired electron location and came to a conclusion that they were localized on the V_1 atoms (in Wadsley notation (*7*)). The electrical conductivity measurements have been mostly carried out in the low-temperature region. High-temperature studies on VOB provided some new information on the nature of this type of compound (*5*, *8*). In the range 650 to 750°K the β-phase of polycrystalline bronzes was found to exhibit semiconductor-metal transition.

The purpose of this work is to study comprehensively the phenomenon by single-crystal electrical conductivity measurements on vanadium bronzes of the type $M_xV_2O_5$ (β-phase), where M = Li, Na, K over the range 300 to 900°K.

Experimental

Preparation of samples. Vanadium oxide bronze samples were synthesized in a platinum dish from vanadium pentoxide ("special grade") and pertinent carbonate ("reagent grade") in the molar ratio $M_2CO_3:V_2O_5 = 1:6$. Mixtures were heated in air atmosphere at 750°C at a rate of 10 to 15°/min. After heating the system was evacuated to a residual pressure of 10^{-1} Torr and the melt was cooled at 5°/min. The resulting solid product had large "blisters" filled with single-crystals. These latter were 10 to 15 mm long and up to 1 mm thick. The X-ray phase examination has shown the thus obtained crystals of VOB to be the β-phase. Their composition is given in Table I. According to the results, the chemical formula of single crystals, given as a unit cell composition, differs from $M_xV_{12}O_{30}$ in oxygen, which is due to crystallization being held in vacuum.

Electrical measurements. The specimen electrical conductivity was measured by d.c. potentiometry with temperature variation at a rate of 1–2°/min in vacuum at a residual

TABLE I

CHEMICAL ANALYSIS DATA FOR SINGLE-CRYSTALS OF VANADIUM OXIDE BRONZES

	Obtained, wt. %			
M	M	ΣV	V^{4+}	Composition
Li	0.98	55.42	7.12	$Li_{1.6}V_{12}O_{29.7}$
Na	3.75	53.40	11.72	$Na_{1.9}V_{12}O_{29.7}$
K	4.30	53.70	7.82	$K_{1.2}V_{12}O_{29.7}$

pressure of 10^{-1} Torr. Measurements were made by passing current along the *b* axis (for crystals $Na_{1.9}V_{12}O_{29.7}$ also perpendicular to the *b* axis) of the crystals and determining the potential drop between two probes mounted on one side of the sample. The potential across the crystal was measured for both current directions to eliminate thermal emfs. Platinum-wire probes, 0.1 mm in diameter, either fused in or pressed against the crystals, were used for potential leads. Samples showed ohmic character up to 100–120 mA. A preliminary study has shown that the way of fixing probes to crystals did not affect the principal results. Sample dimensions and probe separation were measured with a microscope-comparator. Because of uncertainty in determining the exact probe separation and sample dimensions, the estimated error in the conductivity values is 30 percent. The crystals were suspended on platinum-wire probes in order to exclude contact between the specimens and the materials of the measuring cell owing to high temperature. Before measurements, the crystals as mounted in the measuring cell were annealed in vacuum at temperature 570–600°K. The sample temperature was monitored by a chromel–alumel thermocouple placed close to the crystal.

Results

Temperature dependence of conductivity σ, measured along *b* axis (direction [010]), is shown in Fig. 1 at the first cycle of heating–cooling. Curves $\lg\sigma = f(1/T)$, obtained with temperature increase, are marked here by circles; crosses mean the curves obtained on cooling. Energy activation of conductivity E_a, determined from the equation $\sigma = \sigma_0 \cdot \exp(-E_a/kT)$, is equal to 0.065–0.095 eV (Table II) at the initial parts of the curves $\lg\sigma = f(1/T)$. From 650 to 750°K the activation energy first rapidly increases to become 3 to 5 times greater and then drops as with polycrystalline specimens (*5*, *8*). Above 750°K the conductivity changes from semiconducting to metallic. On cooling a significant σ hysteresis is observed and the metallic conductivity is retained down to ~340°K, where σ sharply decreases by a factor of 4 to 30. (A slight slope of the curves $\lg\sigma = f(1/T)$ in Fig. 1(a, c) is a result of residual components of the conductivity tensor other than that along the *b* axis.) During the next cycles, the jump of conductivity is retained for both reheating and recooling, and hysteresis of σ-jump temperature amounts to 3–4 degrees (Fig. 2). It is necessary to note that if at the first cycle of heating–cooling the sample is not heated above 620–650°K, hysteresis σ is not observed

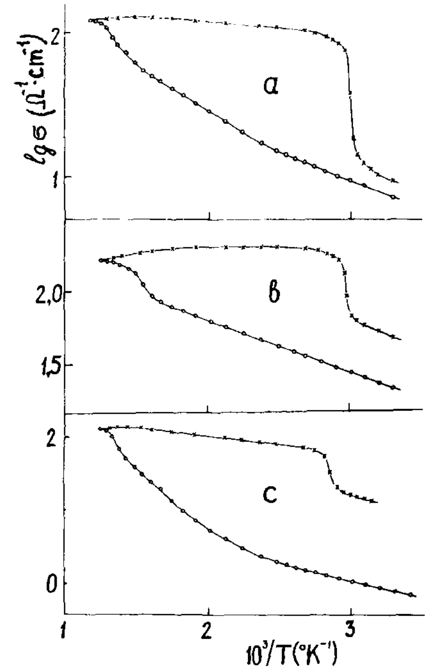

FIG. 1. Electrical conductivity vs reciprocal temperature along the *b* axis for single-crystals: (a) $Li_{1.6}V_{12}O_{29.7}$; (b) $Na_{1.9}V_{12}O_{29.7}$; (c) $K_{1.2}V_{12}O_{29.7}$; (o) heating; (×) cooling.

TABLE II

ELECTRICAL PARAMETERS FOR SINGLE-CRYSTALS OF VANADIUM OXIDE BRONZES

Composition	$\sigma_{\parallel}$ (293°K), $\Omega^{-1}\text{cm}^{-1}$	$E_a{}^{\parallel}$ (293°K), eV	$E_a{}^{\parallel}$ (720°K), eV	$\sigma_{\perp}$ (293°K), $\Omega^{-1}\text{cm}^{-1}$	$E_a{}^{\perp}$ (293°K), eV	T_{tran} °K
$Li_{1.6}V_{12}O_{29.7}$	6.25	0.080	0.28	—	—	333
$Na_{1.9}V_{12}O_{29.7}$	20	0.065	0.29	0.36	0.100	339
$K_{1.2}V_{12}O_{29.7}$	0.56	0.095	0.36	—	—	348

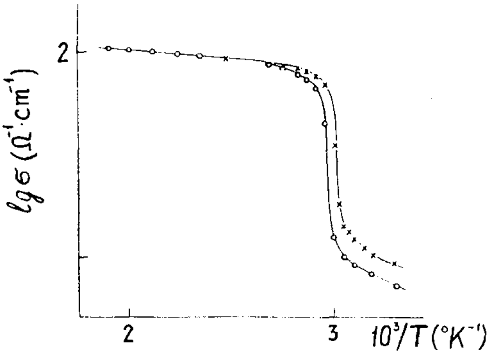

FIG. 2. Conductivity along the b axis for single-crystal of $Li_{1.6}V_{12}O_{30}$ for repeated (cycle of) heating and cooling; (o) heating; (×) cooling.

on cooling. In this case σ-jumps are also absent in the range ~340°K.

Temperature dependence of electrical conductivity perpendicular to the b axis (direction $[10\bar{1}]$) was studied on the bronze $Na_{1.9}V_{12}O_{29.7}$. In this case the activation energy $E_a{}^{\perp}$ is greater than $E_a{}^{\parallel}$ parallel to direction [010] (Table II). High-temperature transformation is realized in two stages; $E_a{}^{\perp}$ has two maxima: $E_a{}^{\perp} = 0.23 \pm 0.01$ eV (650°K) and $E_a{}^{\perp} = 0.29 \pm 0.02$ eV (760°K). Metallic conductivity is attained only above 800°K (Fig. 3). The shape of the curve $\lg\sigma_{\perp} = f(1/T)$ obtained for the cooling stage differs markedly from that for direction [010]. Though in this case the hysteresis of $\sigma_{\perp}$ is evident, the jump in $\sigma_{\perp}$ in the region of 340°K is not observed.

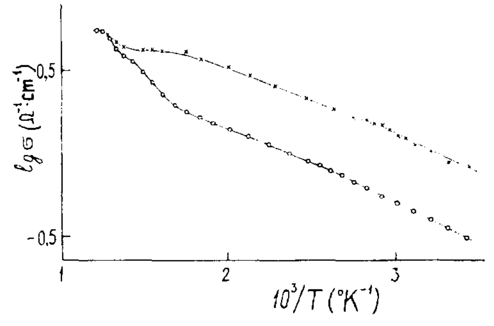

FIG. 3. Conductivity along the direction $[10\bar{1}]$ for single-crystal $Na_{1.9}V_{12}O_{29.7}$: (o) heating; (×) cooling.

Discussion

The nature of VOB monocrystal electrical conductivities in the range of 77–500°K has been discussed earlier in other publications (*4*, *9*). That is why we do not discuss here the low temperature part of the graphs $\lg\sigma = f(1/T)$, but we shall examine the effects at high temperature. Using the energy-level diagram for V^{4+} ion, Perlstein and Sienko (*4*) predicted a sharp increase in the conductivity of VOB at high temperatures due to charge transfer through the high-lying energy levels. In this case, however, a significant hysteresis of electrical conductivity remains unaccounted for.

It was shown earlier that VOB evolve some amount of oxygen (*8*) on heating to 730–780°K. (The fact of significant loss of weight in the solid phase on heating was stated in (*10*)). The amount of evolved oxygen was estimated by independent methods (thermogravimetric and with the help of measurement of equilibrium pressure O_2 over sample). It turned out that no more than 0.7 atoms of oxygen (*8*) are evolved from one elementary cell of bronze. Such insignificant stoichiometry change on oxygen does not lead to appearance of other-phase impurities, but significantly modifies the physical properties of the crystals. Electrical conductivity of crystals along *b* axis assumes metallic character over a wide temperature range (Fig. 1). At the same time, such an effect in the direction perpendicular to *b* axis is not observed (Fig. 3).

The data obtained allow one to account for temperature dependence of electrical conductivity for the polycrystalline specimens of vanadium bronzes (*5*, *8*). Since $\sigma_\perp$ is two orders of magnitude lower than $\sigma_\parallel$, the electrical conductivity in polycrystalline specimens VOB is mainly determined by crystallites in which the *b* axis makes an angle of about 90° with the current direction. Therefore the function $\sigma = f(T)$ for polycrystalline specimens should be similar to $\sigma_\perp = f(T)$. This similarity shows up most vividly for relatively low temperatures. $\sigma_\perp$, however, increases more rapidly with temperature and in the range 700 to 900°K the contribution of $\sigma_\parallel$ to the total conductivity noticeably increases. As a result, only one maximum of activation energy occurs on the curves $\lg\sigma = f(1/T)$ obtained for polycrystalline specimens. Cooling brings no essential variations in $\sigma_\parallel$ whereas $\sigma_\perp$ decreases and, hence, the total conductivity of the specimen will mainly be determined by $\sigma_\perp$. In the region of 340°K the $\sigma_\parallel$ contribution to the total conductivity is insignificant and the jump in $\sigma_\parallel$ exerts almost no effect on the total dependence $\lg\sigma = f(1/T)$.

Sienko *et al.* (*4*, *11*) discussed the possibility of the Mott-transition in vanadium bronzes. Using the Mott criteria (*12*), they drew a conclusion that when the carrier density is over 4.2×10^{21} cm^{-3} the β-phase should exhibit metallic behavior. The number of conduction electrons in the lithium and the sodium VOB obtained in the present study exceed this value (Table 1) but the crystals are semiconductors. Annealing in vacuum at 800° increases electron density by 5–7% (*8*) due to oxygen evolution and the anisotropic semiconductor–metal transition is observed. The increase in electron density is, evidently, not the only reason for this transition. The X-ray examination shows a noticeable decrease in lattice spacings of the bronzes over the range 650–750°K and the Laue patterns indicate a higher degree of perfection. Such a compression of the crystal lattice is retained when the specimen is cooled to room temperature (Table III). According to these data the origin of the semiconductor–metal transition is the decrease in the unit-cell dimensions which results in greater overlapping of the *d*-orbitals of the vanadium ions.

Figure 4 shows a section of the idealized structure of the β-phase. V_1–V_2'–V_1 and V_2–V_1'–V_2 atoms form zigzag chains extending along the *b* axis. Before annealing, the distance between the V atoms in chains is 3.12 Å and that between the chains amounts to 3.49 Å (*7*). Since these values exceed 2.94 Å, activation of the conductivity should be observed (*13*). The compression of the crystal lattice due to partial oxygen evolution from 650° to 750°K may decrease the V–V distance in the chains and lead to metallic conductivity parallel to the *b* axis.

TABLE III

CELL-UNIT PARAMETERS OF VANADIUM OXIDE BRONZES

Composition	Parameter			
	a, Å	*b*, Å	*c*, Å	*β*, degree
	Before annealing			
$Li_{1.6}V_{12}O_{29.7}$	10.10	3.61	15.36	110.28
$Na_{1.9}V_{12}O_{29.7}$	10.09	3.61	15.44	109.62
$K_{1.2}V_{12}O_{29.7}$	10.14	3.60	15.73	109.50
	After annealing			
$Li_{1.6}V_{12}O_{29.7}$	10.00	3.62	15.12	109.03
$Na_{1.9}V_{12}O_{29.7}$	9.98	3.62	15.26	108.92
$K_{1.2}V_{12}O_{29.7}$	9.98	3.61	15.50	108.67

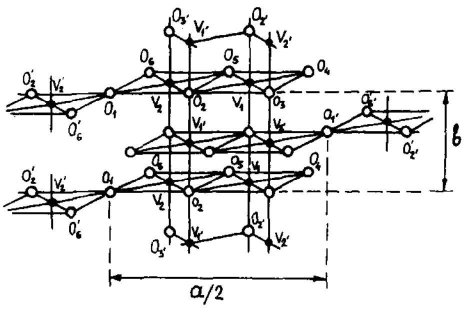

FIG. 4. A section of the idealized structure of $M_{0.33}V_2O_5$ ($M_2V_{12}O_{30}$). This figure is taken from (*6*).

VOB single-crystals annealed in vacuum exhibit a reversible semiconductor–metal transition in the region of about 340°K only along the direction [010] (Figs. 2, 3). It should be noted that the jump temperature varies linearly with ionic radius of the alkali metal.

Contrary to the case of vanadium dioxide (*14*), a jump in the β-phase conductivity brings no change in carrier density. Hence, the semiconductor–metal transition may be caused by vanishing of the activation energy of the conduction–electron mobility. In this case a jump in σ is defined by $\exp\cdot(E_a/kT_{\text{tran}})$, where E_a is the activation energy for conductivity on the semiconductor side of transition, T_{tran} is the temperature of the conductivity jump. Experimental values of E_a and T_{tran} (Table II) give $\exp\cdot(E_a/kT_{\text{tran}}) = 10\text{–}30$. The agreement with the results of the measurements (4 to 30) supports the suggested mechanism of semiconductor–metal transition in the region of 340°K. The precision X-ray examination of the sodium vanadium bronze showed that for this transition the change in unit-cell volume, if any, is less than 0.07%. This fact together with a slight broadening of the transition over a range of temperature and insignificant hysteresis of T_{tran} (3 to 4°) speak in favor of a second-order transition. Indeed, the specific heat measurements of annealed-in-vacuum $Na_{1.9}V_{12}O_{29.7}$ crystals showed an anomaly of λ-peak-form (*15*). The temperature of the anomaly was 334.2°K. Graphic analysis of the specific heat confirmed that at this temperature a second-order phase-transition occurs. Evidently, a slight shift of the atoms V_1, V_2', V_1 and V_2, V_1', V_2 occurs near T_{tran} in the planes perpendicular to the *b* axis, which is responsible for appearance and vanishing of potential barrier for electrons. The existence of alkali ions, differing in size and electron structure, in the crystal "tunnels" may influence the temperature of the above vanadium-atom displacement in agreement with the obtained data on electrical conductivity of VOB.

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