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Abstract

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SEMICONDUCTING PROPERTIES OF VANADIUM AND NIOBIUM PENTOXIDES IN THE SOLID AND LIQUID STATES

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The great importance of semiconductors in the electrochemistry (1) of molten oxides (2) and the scarcity of experimental data for solid and liquid oxides V_2O_5 and Nb_2O_5 prompted us to carry out measurements of the specific electrical conductivity χ, the thermoelectromotive force (t.e.m.f.), and the Hall constant R_X.

The polytherms of χ are presented in Fig. 1. The relatively high values of χ and the absence of a jump on melting indicate that V_2O_5 and Nb_2O_5 are semiconductors in both aggregate states.

Table 1

Activation energies of conductivity $\Delta\varepsilon$, t.e.m.f. coefficients, and other characteristics of V_2O_5 and Nb_2O_5

	V_2O_5	V_2O_5	Nb_2O_5	Nb_2O_5
	600° (solid)	1000° (liq.)	1200° (solid)	1500° (liq.)
χ, Ω^{-1} cm^{-1}	0.25	1.83	0.12	3.61
$\lg \chi_0$	1.94	3.70	2.72	6.30
$\Delta\varepsilon \cdot 10^{12}$, erg	1.58	2.73	3.56	6.42
n, cm^{-3} $\{n_1$	$7.0 \cdot 10^{17}$	$9.16 \cdot 10^{16}$	$3.5 \cdot 10^{16}$	$7.3 \cdot 10^{14}$
n, cm^{-3} $\{n_2$	$4.1 \cdot 10^{16}$	$1.13 \cdot 10^{16}$		
u, $\frac{\text{cm}^2}{\text{V} \cdot \text{sec}}$ $\{u_1$	2.2	–	22	–
u, $\frac{\text{cm}^2}{\text{V} \cdot \text{sec}}$ $\{u_2$	38	$\{u_n$ 33		
u, $\frac{\text{cm}^2}{\text{V} \cdot \text{sec}}$		$\{u_p$ 189		
α_{theor}, $\frac{\mu\text{V}}{\text{deg}}$ $\{\alpha_1$	820	–	1100	–
α_{theor}, $\frac{\mu\text{V}}{\text{deg}}$ $\{\alpha_2$	1030	–		

Fig. 1. Dependence of the specific electrical conductivity $\varkappa$, the differential thermoelectric power α, and the thermoelectric power of the galvanomagnetic effect V_x on temperature for V_2O_5 (curves 1) and Nb_2O_5 (curves 2)

Figure 1: Fig. 1. Dependence of the specific electrical conductivity $\varkappa$, the differential thermoelectric power α, and the thermoelectric power of the galvanomagnetic effect V_x on temperature for V_2O_5 (curves 1) and Nb_2O_5 (curves 2)

	V_2O_5	V_2O_5	Nb_2O_5	Nb_2O_5
$\alpha_{\text{exp}}, \frac{\mu\text{V}}{\text{deg}}$	700	200	950	220

As is seen from Table 1, the activation energies of conductivity, calculated from the equation $\chi = \chi_0 \exp\{-\Delta\varepsilon/2kT\}$, are noticeably larger for molten V_2O_5 and Nb_2O_5 than for the solid substances. It may be supposed that in the former case intrinsic conductivity predominates, while in the latter it is impurity conductivity.

At temperatures below 0° the electrical conductivity of V_2O_5 is very small (at $T = -30^\circ$, $\chi \cong 10^{-5}$, $\Delta\varepsilon = 0.72 \cdot 10^{-12}$ (^{3})) and is determined by accidental impurities. At sufficiently high temperatures impurities arise as a result of partial dissociation of V_2O_5 to lower oxides, and the activation energy increases. For example, according to (^{4}), at 430° $\Delta\varepsilon = 1.56 \cdot 10^{-12}$, which is close to the value obtained by us at 600° (see Table 1). It also follows from the table that $\Delta\varepsilon$ for Nb_2O_5 is greater than for V_2O_5. It is possible that, in the region of intrinsic conductivity, this is due to the stronger bond between the atoms O and Nb. It is known (^{5}) that for a number of elements and alloys (Si, Ge, GaSb, InSb, CaAs, and others) the value of $\Delta\varepsilon$ increases together with the binding energy between the particles.

The values found for $\Delta\varepsilon$ were used to estimate the number of current carriers n. Their magnitude (n_p) for the solid state was calculated from equation (6)

$$n_\text{p} = V\overline{N}_\text{p}\sqrt{\frac{2(2\pi m_n kT)^{3/2}}{h^3}}\, e^{-\Delta\varepsilon/2kT}. \tag{1}$$

The effective mass of the electron m_n was taken equal to the rest mass (m_0). The number of impurity centers N_p was set equal to the number of cations of lower valence, which was determined from chemical-analysis data. The value of n_p thus found for V_2O_5 differs somewhat from those calculated from data of other authors, probably because the samples were studied at different temperatures ($T = 130^\circ$, $n_\text{p} = 0.9 \cdot 10^{17}$ [4]; $T = 1000^\circ$, $n_\text{p} = 1.6 \cdot 10^{17}$; $T = 1100^\circ$, $n_\text{p} = 0.6 \cdot 10^{18}$ [7]) and had different histories.

Fig. 1. Dependence of the specific electrical conductivity $\varkappa$, the differential thermoelectric power α, and the thermoelectric power of the galvanomagnetic effect V_x on temperature for V_2O_5 (curves 1) and Nb_2O_5 (curves 2)

Since, in the case of impurity conduction, the quantity $\varkappa$ is determined by only one type of current carrier, their mobility u_n was calculated from equation (6)

$$\varkappa = neu_n. \tag{2}$$

It turned out that the values of u_n for Nb_2O_5 approach those in the oxides Cu_2O and ZnO ($u \approx 100$ [6]), while for V_2O_5 they are comparable with the mobility in TiO_2 ($u \approx 1$ [8]).

In the molten state, where intrinsic conductivity predominates, the number of carriers was approximately estimated from the formula for crystals [6]:

$$n = \frac{2(2\pi m_n kT)^{3/2}}{h^3}\, e^{-\varepsilon/2kT}. \tag{3}$$

This may be justified by the fact that the conditions for the formation of free electrons in solid and liquid bodies are determined mainly by the short-range order in the arrangement of atoms.

Figure 1 shows the dependence of the thermoelectric power on the mean temperature

$$\left(\frac{T_\mathrm{g} + T_\mathrm{x}}{2}\right).$$

In all cases the more strongly heated part of the sample was charged positively. In other words, V_2O_5 and Nb_2O_5 (in contrast to the results—

there (7)) have electronic conductivity. For V_2O_5 this is confirmed by the data of (^{3,4}), as well as by measurement of the thermoelectric power in glasses with a high content of V_2O_5 (^{9}). Electronic conductivity should have been expected here, since a stoichiometric excess of metal in sulfides and oxides promotes the formation of donor levels (^{6}).

The magnitude of the thermoelectric power for impurity semiconductors can be calculated from the equation (^{6})

$$\alpha = \frac{k}{e}\left[r + 2 + \ln\frac{2(2\pi m_n kT)^{3/2}}{n\,h^3}\right], \tag{4}$$

in which $r = 2$ for scattering of electrons by impurity ions. Substituting into (4) the values of n , determined from the data on χ, we find values of α_theor close (see Table 1) to the experimental α_exp.

The decrease of the thermoelectric power with increasing temperature permits one to suppose that, on passing from impurity to intrinsic conductivity, the diffusion of electrons is partly compensated by the flux of holes. The latter circumstance seems somewhat unusual, since in the presence of intrinsic conductivity the number of free electrons formed, n, is equal to the number of holes p in the valence band ($n = p$), while the mobility u_n is, as a rule, greater than u_p.

However, a number of so-called anomalous semiconductors are known in which, in the region of intrinsic conductivity, $u_p > u_n$, for example Mg_3Sb_2, $ZnSb$ (^{10}). To explain the drop in the thermoelectric power upon melting of V_2O_5 and Nb_2O_5, which possess electronic conductivity, one must suppose that they also are anomalous.

With the method used by us (see also (^{11})), the measured thermoelectric power is composed of two quantities: the difference of the electrode potentials at the boundaries Pt | melt (heterogeneous effect) and the potential drop between the hot and cold ends of the specimen (homogeneous effect). The heterogeneous effect can be estimated, assuming that Pt is an oxygen electrode, from the equation (^{12})

$$\alpha_{\text{het}} = \frac{1}{4F}\left[\int_0^T C_{O_2}\frac{dT}{T} - \int_0^T \frac{2}{7}C_{V_2O_5}\frac{dT}{T}\right]. \tag{5}$$

Taking the values of the heat capacities C_{pO_2} and $C_{pV_2O_5}$ from (^{13}), we find α_{het} (l) $= 325$ and α_{het} (s) $= 394\,\mu$V/deg. Subtracting them from the measured thermoelectric powers, we have α_{hom} (l) $= -125$, α_{hom} (s) $= 300\,\mu$V/deg. Thus, that part of the thermoelectric power which is due to diffusion of current carriers inside the specimen (α_{hom}) changes its sign when V_2O_5 passes into the liquid state.

What has been said is confirmed by measurements of the galvanomagnetic effect. From Fig. 1 it is seen that the Hall constant:

$$R_X = \frac{V_X\,(\text{V})\,a\,(\text{cm})}{I\,(\text{A})\,H\,(\text{oersted})}\cdot 10^8\ \frac{\text{cm}^3}{\text{coulomb}} \tag{6}$$

decreases with decreasing temperature and changes sign on passing through the melting point of V_2O_5 (670°). Since in the region of intrinsic conductivity

$$R_X = -\frac{3\pi}{8}\frac{1}{ne}\frac{u_n - u_p}{u_n + u_p}, \tag{7}$$

the negative sign of R_X indicates electronic conductivity of solid V_2O_5, and the change of sign on melting indicates that u_p has become greater than u_n.

Using the value of the Hall constant, one can estimate in another way the number of carriers n_2 and their mobility u_2. For solid V_2O_5 the value n_2 was determined from the relation

$$R_X = -A\frac{1}{ne}, \tag{8}$$

where $A = 1.93$ for scattering of electrons by impurity ions. Then u_2 and α_2 were calculated from formulas (2) and (4). The values of n_2, u_n, and u_p for molten $\mathrm{V_2O_5}$ were found at 800° from equations (7), (9), and (10) (6)

$$\kappa = en(u_n + u_p); \tag{9}$$

$$\frac{u_n}{u_p} = \frac{\dfrac{\Delta\varepsilon}{2|e|} - \dfrac{\Delta\alpha}{\Delta(1/T)}}{\dfrac{\Delta\varepsilon}{2|e|} + \dfrac{\Delta\alpha}{\Delta(1/T)}}. \tag{10}$$

The values n_2 obtained for $\mathrm{V_2O_5}$ (see Table 1) are an order of magnitude smaller than n_1. The discrepancy for solid $\mathrm{V_2O_5}$ is partly due to the lower degree of dissociation of $\mathrm{V_2O_5}$ in determining the galvanomagnetic effect, since in this case the melt temperature did not exceed 850°. If n_2 is compared with n_1 calculated for the specimen in which measurements were carried out up to 1000° (see above), the difference is smoothed out. However, the main reason for the difference between n_1 and n_2 for the solid and liquid states is that, in the calculations of n_1, we assumed $m_n = m_0$. Now, taking $n_1 = n_2$, m_n can be estimated from formulas (1) and (3). It turned out that the effective mass of the electron is appreciably smaller than the rest mass and is approximately equal to $m_n \simeq 0.3m_0$.

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Note: Figure translations are in progress. See original paper for figures.

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