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Electrical conductivity of α-$H_XV_2O_5$ ($X = 0.00$–0.27): dependence of hydrogen concentration and orientation

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The dependence of the electrical conductivity, σ, on the hydrogen concentration and crystallographic orientation has been investigated using single crystals of $H_xV_2O_5$, which were grown by the Bridgeman method and doped with hydrogen within the solid solubility in the α phase by the spillover technique. The temperature dependence of σ showed the feature of diffusive hopping of thermally activated electrons above ~180 K and variable range hopping below ~180 K. The dependence of σ on the crystallographic orientation was little different from that of V_2O_5. The change in σ with the hydrogen concentration was not monotonic; σ increases with x up to $x \simeq 0.06$, but decreases above $x \simeq 0.06$. This behaviour can be explained based on the competition between the increase in the carrier density and the depression of the mobility of carriers with increasing x.

1. Introduction

It is well known that, as shown in Fig. 1, V_2O_5, an orthorhombic semiconductor, has two-dimensional networks of columnar spaces and vanadium atom arrays in a zigzag chain. The columnar space can accommodate various kinds of metallic elements, such as lithium [1], sodium [2, 3], copper [4], silver [5], lead [6], thallium [7], and zinc [8]. With increasing dopant concentration, the crystal structure becomes distorted and changed into the monoclinic β phase, β-$M_xV_2O_5$. The excess electron released from a dopant contributes to the electrical conductivity by hopping along the vanadium chains which are distorted but still remain in the β phase.

The accommodation of those metallic elements often causes large changes in the physical properties, which have been observed by measurements of the electrical conductivity [9–14], nuclear magnetic resonance [15–17], electron spin resonance [18–20], specific heat capacity [21, 22], and optical properties [23–25]. These experiments have clarified that V_2O_5 is originally a narrow-band semiconductor and that metal dopants supply their valence electrons to the matrix as carriers. The latter fact is confirmed by zero Knight shift in nuclear magnetic resonance (NMR) measurements.

Those excess electrons are located on vanadium sites by changing V^{5+} ions into V^{4+} ions and strongly correlate with the lattice through an ionic Coulomb field from the lattice, which causes the formation of small poralons with 1/2 spin, localized electrons accompanied by local distortion of the lattice. The electrical conduction in β-$M_xV_2O_5$ is considered to be brought about by hopping of polarons. With increasing polaron density, the probability that a polaron finds another one on its nearest neighbour increases, and accordingly, if the lattice is soft enough to cause a local deformation for overcoming the Coulombic repulsion, such a pair of polarons is expected to form a coupled state, a bipolaron. It was theoretically predicted by Anderson [26], Chakraverty *et al.* [21], and Alexandrov and Ranninger [27] in the β-$M_xV_2O_5$ system, and the experimental evidence was later obtained by NMR and X-ray diffraction (XRD) measurements in β-$Na_{0.40}V_2O_5$ [28, 29] and β-$Ag_{0.40}V_2O_5$ [30].

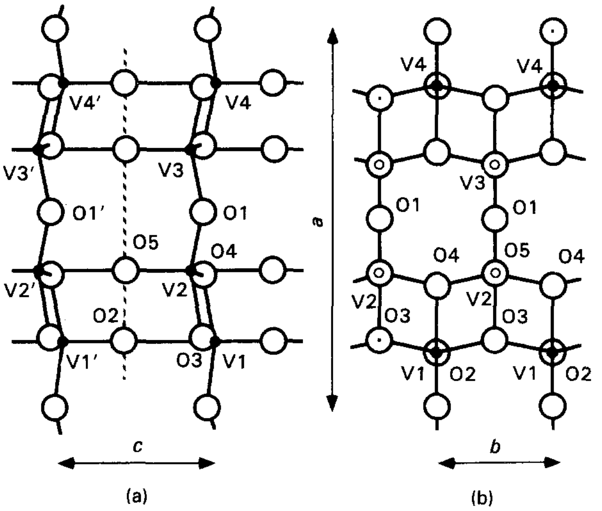

Figure 1 Atomic arrangements in the V_2O_5 lattice. (a) Projection on to the *a–c* plane, (b) Projection on to the *a–b* plane. (○) oxygen atom (○, ●) vanadium atoms. The columnar spaces which extend like a two-dimensional network can be seen as a cavity surrounded by O_5, O'_1, O_5 and O_1 in (a) and by O_2, O_1, O_4 and O_1 in (b).

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Hydrogen is an atom with the smallest atomic radius and capable of charging up to + 1 in the same way as are alkali metals. Recently, several studies on $H_xV_2O_5$ including absorption dynamics [31–33], crystallographic change by XRD [34, 35], and NMR, electron spin resonance (ESR) and infrared (IR) spectra [31, 36] has been reported. They are, however, mostly on heavily doped ones, β-$H_xV_2O_5$ and γ-$H_xV_2O_5$; studies on the α range have scarcely been reported.

In the present paper, we report a brief summary of our experiments on the electrical conductivity, σ, of α-$H_xV_2O_5$ single crystals for several hydrogen concentrations. The dependence of σ on the hydrogen concentration, x, is discussed based on the competition between an increase in the carrier density and a depression effect on the mobility due to bipolarons, both of which are supposed to grow with increasing x.

2. Experimental procedure

2.1. Specimen preparation

Single crystals of V_2O_5 were grown by the Bridgeman method: V_2O_5 powder (CERAC, purity better than 99.9%), encapsulated in an evacuated silica tube, was heated from its corn-shaped end by passing through a vertical furnace at a speed of 4 cm h^{-1}. The furnace had a temperature gradient of 13 °C cm^{-1} at the position of 674 °C, the melting point of V_2O_5. A single crystal thus obtained had the dimensions ~ 3 × 10 × 1 mm^3 for measurements of the electrical conductivity, and was then doped with hydrogen up to a given concentration between $x = 0.0$ and 0.27 by the spillover technique [37]. All the specimens used in the present investigation were in the α phase. This is confirmed by XRD measurements [38], which showed that the solid solubility in the α phase was ~ 0.40 at ambient temperature.

2.2. Measurements of electrical conductivity

The electrical conductivity along the a and b axes was measured over a temperature range 77–300 K by the four-terminal method. For the c axis, the Montgomery method [39] was adopted, because our specimens were too thin along the c axis to attach electrodes for the four-terminal measurements.

3. Results

3.1. Electrical conductivity

Fig. 2 shows the temperature dependence of the electrical conductivity along the three crystal axes. As typical examples, the results for $x = 0.00$ and 0.20 are presented. For both of the cases, the ratio $\sigma_b:\sigma_a:\sigma_c$ (σ_a, for example, denotes the electrical conductivity along the a axis) is roughly 170:20:1 and almost independent of temperature. The absolute value of each σ_i($i = a$, b and c) for $x = 0.20$ is a little smaller than that for $x = 0.00$. The relation ln (σT) against $1/T$ for both $x = 0.00$ and 0.20 is linear above ~ 180 K for all the directions; the electrical conductivity is shown in the form of

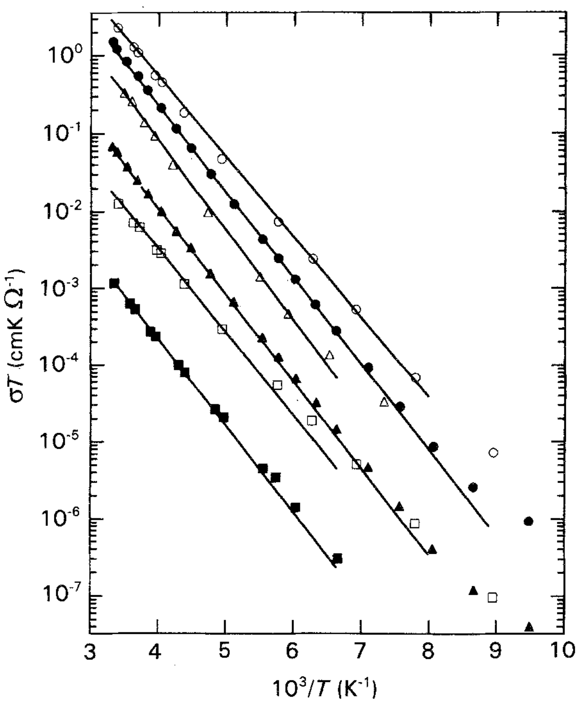

Figure 2 Orientation and temperature dependence of the electrical conductivity σ. Logarithmic plots of σT are shown as a function of $1/T$ for (○, △, □) V_2O_5 and (●, ▲, ■) $H_{0.20}V_2O_5$. (○, ●) Parallel to b, (△, ▲) parallel to a, and (□, ■) parallel to c.

$$\sigma \propto \frac{1}{T}\exp\left(-\frac{E_a}{k_B T}\right) \qquad (1)$$

where E_a is the activation energy for diffusive hopping of isolated electrons and k_B is Boltzmann's constant. The value of E_a obtained from Fig. 2 is 0.21–0.22 eV for $x = 0.00$, and 0.22 eV for $x = 0.20$, both depending little on the orientation.

On the other hand, the dependence below ~ 180 K appears to be a feature of the variable range hopping, which follows the relation

$$\sigma = \sigma_0 \exp\left[-\left(\frac{E}{k_B T}\right)^{\frac{1}{n+1}}\right] \qquad (2)$$

The conduction by thermally activated electrons is thus gradually replaced by the tunnelling-ruled conduction with decreasing temperature. The dimension of the variable range hopping, n, is found to be 1 for most of the cases, though $n = 3$ seems to be good for some cases.

It should be remarked here that the transition from a high to a low-temperature region is commonly observed for any hydrogen concentration but that the critical temperature is not very clear and ranges from 200–140 K. Therefore, we express the transition temperature as ~ 180 K for the sake of convenience.

The dependence of σ_i on x at 250 K is shown in Fig. 3. It is clear that σ_b does not change monotonically with x; with increasing x, σ_b shows a tendency to increase until x-0.06 and then decreases. Similar tendencies are also observed for σ_a and σ_c.

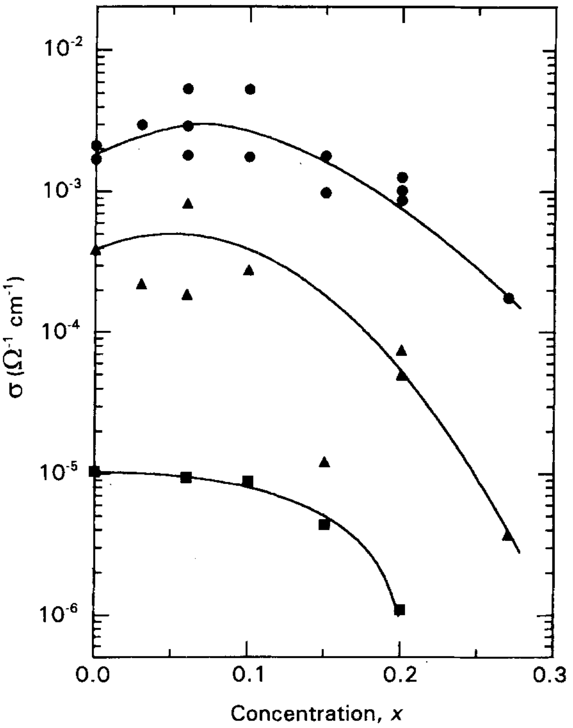

Figure 3 Dependence of the electrical conductivity, σ, at 250°C on the hydrogen concentration. The solid lines are shown as a guide for the eye. (●) Parallel to *b*, (▲) parallel to *a*, (■) parallel to *c*.

4. Discussion

The large anisotropy of the electrical conductivity is explained as follows. Because the activation energies obtained for the three directions are almost identical to each other, the origin of the anisotropy should be attributed to *C* in Equation 1, a temperature-independent factor of the mobility in the hopping-ruled conduction. Considering the low conductivity and the large anisotropy, it appears that thermally activated electrons move by hopping along vanadium chains which run parallel to the crystal axes; V_1–V_2–V_1 V_1–V_2–(O_1)–V_3–V_4–(O_1)–V_1 and V_1–(O_2)–V'_1–(O_2)–V_1 for the *a*, *b* and *c* directions, respectively (see Fig. 1 for the geometrical configurations and note that V_3–V_4 is crystallographically equivalent to V_1–V_2). If this is the case, the mobility along each direction would be dominated by the electron hopping between the pair of vanadium atoms which is the largest in distance along the corresponding path (V_1–V_2, V_2–(O_1)–V_3 and V_1–(O_2)–V'_1 for the *a*, *b* and *c* directions, respectively).

The hopping probability is given as a function of the overlap integral, *S* between the wave functions of these neighbouring V–V and/or V–O atoms, which should be independent of temperature and determined by the geometrical configuration. The large anisotropy, therefore, can be attributed to the difference among values of *S* along the crystal axes; the larger is *S*, the easier is the diffusive hopping of the electrons to the neighbouring vanadium sites (V^{5+} ions, in the real sense). The overlap integrals between d–d, d–p, p–p orbitals of the neighbouring V–V and V–O pairs are calculated separately for the atomic configuration of V_2O_5 and summed to give a total one, *S*. The results are shown in Table I. It should be noted that the overlap integral between O 2p and V dε was small enough to be neglected. It is clear that the summed *S* is largest along the *b* axis, second along the *a* axis, and smallest along the *c* axis. This order in the magnitude of *S* is consistent with the observed anisotropy of electrical conductivity.

TABLE I Sum of overlap integrals between 3d–3d, 3d–4p, and 4p–4p wave functions of two neighbouring vanadium atoms. The site of each vanadium atom is shown in Fig. 1

Direction	Atoms	*S*
‖*b*	V_1–V_2	0.278
‖*a*	$V_2 - V_3$	0.154
‖*c*	$V_1 - V'_1$	0.037

The dependence of σ on *x* shown in Fig. 3 can be explained by the competition of two phenomena, the increase of the carrier density and the formation of bipolarons. At small *x*, most of the carriers are considered to exist as single polarons which are mobile in the crystal. The number of carriers is propotional to *x*, and accordingly, σ increases with increasing *x* in the lower concentration range. However, the more single polarons increase in number, the more the formation of bipolarons is promoted through the interaction between single polarons. As seen in β-$Na_{0.33}V_2O_5$, bipolarons should be formed on the closest pair of the vanadium sites, V_1–V_2 in the present case, and less mobile than single polarons in terms of energy. This is because a bipolaron requires a larger energy for a jump than a single polaron, and because the movement of a bipolaron is restricted in a vanadium chain on which it exists. In addition, this inactive bipolaron functions as a blockage for single polarons and prevents them from hopping around by decreasing the chance of finding hopping destinations. The increase in bipolarons, therefore, not only suppresses the increment of single polarons but causes the increase in the resistance to carrier motion. Consequently, σ decreases with increasing *x* in the higher concentration range.

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