

# Optical Properties, Electronic Structure and Magnetism of $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$

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The optical properties of sodium-deficient  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  ( $0.85 \leq x \leq 1.00$ ) single crystals are analyzed using ellipsometry, and infrared reflectivity techniques. In sodium deficient samples, the optical absorption peak associated to the fundamental electronic gap develops in the middle of the pure  $\alpha'$ - $\text{NaV}_2\text{O}_5$  gap at  $\sim 0.44$  eV, and the material remains insulating up to the maximal achieved hole concentration of about 15%. Nonmetallic behavior under hole doping provoked reinterpretation of the  $\alpha'$ - $\text{NaV}_2\text{O}_5$  optical spectra. We argue that the absorption peak at about 0.9 eV corresponds to the photoionization energy of a large polaron.

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**KEY WORDS:**  $\text{Na}_x\text{V}_2\text{O}_5$ ; optical conductivity; polarons.

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## 1. INTRODUCTION

$\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  belongs to the family of  $\text{AV}_2\text{O}_5$  oxides (A = Li, Na, Ca, Mg) which have demonstrated, due to their peculiar crystal structures [1,2], a variety of low-dimensional phenomena. The nominally pure  $\alpha'$ - $\text{NaV}_2\text{O}_5$  is a mixed valence compound ( $\text{V}^{4+} : \text{V}^{5+} = 1:1$ ), with the structure consisting of vanadium–oxygen ( $\text{VO}_5$ ) pyramids that are connected via common edges and corners to form layers in the (*ab*) plane. Its structure can be described as an array of parallel ladders running along the *b*-axis, Fig. 1. Each rung is made of a V–O–V bond, and contains one valence electron donated by the sodium atoms which are situated between layers. The sodium deficiency does not alter  $\alpha'$  crystal structure [3] up to  $x = 0.70$ , but changes the relative abundance of the  $\text{V}^{4+}$  and  $\text{V}^{5+}$  ions, e.g. introduces “extra” holes (more  $\text{V}^{5+}$  ions) in the (*ab*) planes.

This compound exhibits a phase transition at  $T_c = 34$  K [1,2] that is usually referred to in the literature as the charge-ordering (CO) phase transition. From the mixed-valence point of view its existence is not unusual, since a common consequence of the mixed valence is the appearance of charge-ordering, which is a class of metal–insulator transitions [4]. However, the phase on both sides of the transition in  $\alpha'$ - $\text{NaV}_2\text{O}_5$  are insulators, and a very interesting interplay between charge and spin dynamics results in the phase-transition discovered in this compound.  $\alpha'$ - $\text{NaV}_2\text{O}_5$  is one-dimensional antiferromagnetic (AF) insulator at room temperature [3], despite the fact that the vanadium atoms have uniform valence of +4.5, which indicates the quarter-filled band structure, and suggests a metallic state. However, the optical measurements [5] revealed the electronic gap of the order of 1 eV, which is formed between linear combinations of the  $3d_{xy}$  states of the two vanadium ions forming the rungs [6]. The insulating ground state is argued to originate from the strong electron–electron interaction [6] e.g. due to the presence of a large on-site Hubbard repulsion parameter *U*.

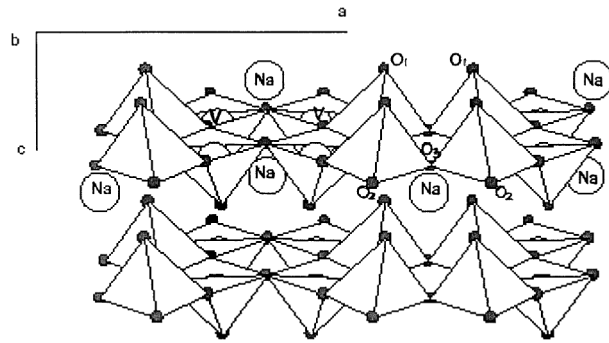
The effects of the hole doping on the optical properties of  $\alpha'$ - $\text{NaV}_2\text{O}_5$  have not been studied in details. This interesting topic deserves attention because of the spectacular effects observed in doped

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**Fig. 1.** Schematic representation of the  $\alpha'$ - $\text{NaV}_2\text{O}_5$  crystal structure.

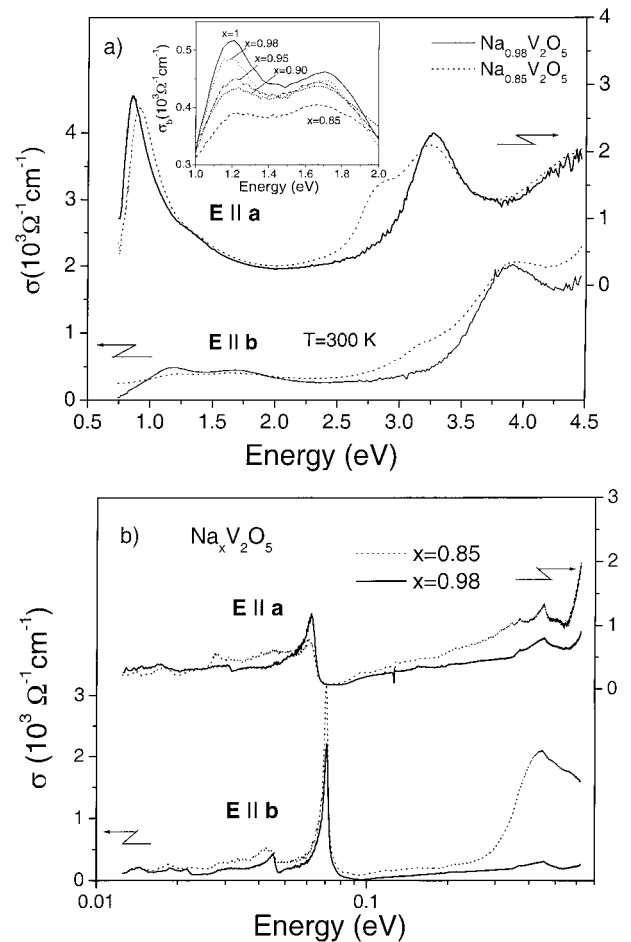
AF insulators, e.g. high-temperature superconductivity. We analyze the influence of the Na-deficiency on the optical transitions in the mid-IR, and visible energy range. First we show that  $\alpha'$ - $\text{NaV}_2\text{O}_5$  remains insulating under hole doping, and demonstrate that such behavior is not consistent with current understanding of optical spectra, and the electronic structure of  $\alpha'$ - $\text{NaV}_2\text{O}_5$ . Second, we argue that the absorption peak at about 0.9 eV corresponds to the photoionization energy of a large polaron.

## 2. EXPERIMENT

The present work was performed on single crystal plates of  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  ( $0.85 \leq x \leq 1.00$ ) with dimensions typically about  $2 \times 4 \times 0.5 \text{ mm}^3$  in the  $a$ ,  $b$ , and  $c$  axes, respectively. The details of the sample preparation were published elsewhere [2]. The ellipsometric measurements on the (001) surfaces of the crystals, both with the plane of incidence of the light along the  $a$  and the  $b$  axis. An angle of incidence  $\theta$  of  $66^\circ$ , was used in all experiments. Procedure for extraction of the dielectric constants is described in Ref. [7]. The infrared measurements were carried out with a BOMEM DA-8 FIR spectrometer. A DTGS pyroelectric detector was used to cover the wave number region from 100 to  $700 \text{ cm}^{-1}$ ; a liquid nitrogen cooled HgCdTe detector was used from 500 to  $5000 \text{ cm}^{-1}$ . Spectra were collected with  $2 \text{ cm}^{-1}$  resolution, with 1000 interferometer scans added for each spectrum.

## 3. RESULTS AND DISCUSSION

The optical conductivity of  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$ , obtained from the ellipsometric measurements is given



**Fig. 2.** Optical conductivity of  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  at  $T = 300 \text{ K}$  for  $E \parallel a$  and  $E \parallel b$  measured with (a) ellipsometry, and (b) infrared reflectance techniques. The  $x = 0.98$  (solid), and  $x = 0.85$  (dashed). Inset:  $\sigma_b$  for various sodium concentrations.

in Fig. 2a. For the nominally pure  $\alpha'$ - $\text{NaV}_2\text{O}_5$  the bands at the energies 0.9, 1.2, and 3.2 eV for  $\sigma_a$ , and at 1.2, 1.6, and 3.7 eV for  $\sigma_b$  are found in accordance with previous reports [8–11]. The sodium deficiency causes the activation of the new optical transitions at about 2.8 eV in  $\sigma_a$  and at 3.2 eV in  $\sigma_b$ , see Fig. 2a, and induces the blue shift of the 0.9 eV peak. On the contrary, the structure at about 1.1 eV in  $\sigma_a$  do not exhibit the energy shift under doping, see inset Fig. 2. This fact suggests that these two structures do not have the same origin.

The optical conductivity, obtained from the Kramers-Kronig (KK) analysis of the IR reflectivity, is presented in Fig. 2b. In both  $\sigma_a$  and  $\sigma_b$  spectra of  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  we found no Drude behavior at low frequencies. Instead, the dominant feature activated by the Na-deficiency is observed in  $\sigma_b$  at about 0.44 eV,

with a half width at half maximum (HWHM) of about 0.25 eV. Note that its energy corresponds to the half of the energy of 0.9 eV peak.

If the Coulomb interaction between sodium ions and rung electrons is neglected the electron properties are governed by the isolated V—O planes. This case is vastly elaborated in the literature [12–15]. The essential features of the  $\alpha'$ - $\text{NaV}_2\text{O}_5$  electronic structure are formed from oxygen 2p and vanadium 3d states. The fully occupied oxygen 2p states are located about 3 eV below the lowest of the V3d states split by ligand field [16]. The lowest state of the  $\text{V}^{4+}$  3d manifold,  $3d_{xy}$  state, is occupied by one electron. The V—O—V rung is formed through the electron hopping via oxygen  $\text{O}_3$  states. Because of this coupling, usually denoted as  $t_a$ , two  $3d_{xy}$  orbital levels form symmetric and antisymmetric combinations of levels (bonding and antibonding levels) that are split by  $2t_a \sim 0.7$  eV. The insulating state appears due to the large on-site Hubbard repulsion,  $U$ , which pushes the Fermi level in the middle of the gap between bonding and antibonding states [6]. Thus, the main peak in the optical spectrum along the  $a$  direction at 0.9 eV seems to originate from the transitions between bonding (B) and antibonding (AB) states of the same rung [7]. Accordingly, the structure at 1.1 eV in  $\sigma_b$  corresponds to the similar transition process along the  $b$  direction. The higher energy bands, above 3 eV, are similar to those found in  $\text{V}_2\text{O}_5$  [17], and correspond to the O2p–V3d type of transitions.

The sodium deficiency changes the relative abundance of the  $\text{V}^{4+}$  and  $\text{V}^{5+}$  ions. In fact, introduction of holes leads to the formation of rungs without electrons, similar to the  $\text{V}^{5+}\text{—O}_3\text{—V}^{5+}$  bonds in  $\text{V}_2\text{O}_5$ . However, previous studies [8–11] did not clearly show what kind of the final state is involved in the 3.2 eV ( $\sigma_a$ ) transition, and this turns out to be the most important information in order to understand the electronic structure of the Na-deficient samples. If the final state is the bonding V3d<sub>xy</sub> state, as described in Ref. [11], the  $\alpha'$ - $\text{NaV}_2\text{O}_5$  should be in the metallic state, which is in strong disagreement with the observed insulating behavior. In the insulating state, the optical transitions between O2p and the bonding V3d<sub>xy</sub> states should be forbidden. The next possibility is that the final state of 3.2 eV peak corresponds to the nonbonding V3d<sub>xy</sub> state, which forms when there are two electrons in the rung. According to the modified Heitler-London model, proposed in order to account for the observed features in the optical conductivity spectra of  $\alpha'$ - $\text{NaV}_2\text{O}_5$  [7], the nonbonding band lies in the middle of the bonding–antibonding

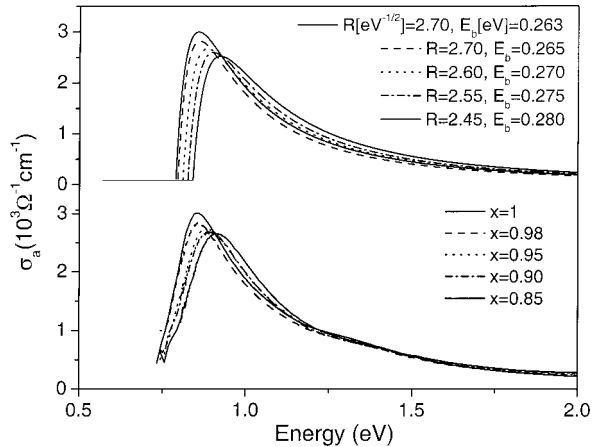
gap. The sodium deficiency is expected to drive the Fermi level inside of the bonding band, which now activates the transitions between the O2p and bonding V3d<sub>xy</sub> states. In this case, the bonding level is partially filled, so this scenario also rely on the formation of the metallic state in  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  which is not observed.

Clearly, all scenarios discussed so far are not yet adequate to fully describe the optical transitions and the electronic structure of the  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$ . In the following, we argue that 0.9 eV peak observed in the absorption spectra of  $\alpha'$ - $\text{NaV}_2\text{O}_5$  originates from the photoionization of a large polaron. By taking the Coulomb interaction between sodium ions and V—O layers into consideration one introduces additional insulating character to the electronic properties of  $\alpha'$ - $\text{NaV}_2\text{O}_5$ , since the electrons are allowed to bound within potential wells produced by sodium atoms. The consequences would be the appearance of electron–lattice interaction, and possibly polaron formation. Existence of strong electron–phonon interaction has been confirmed with the Raman spectra [18,19]. The confirmation for a “strong” insulating behavior come from our IR spectra (see Fig. 2) as well as from the transport measurements [3] of sodium-deficient samples,  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$ . Despite large hole doping, the insulating state persists up to the maximal achieved hole concentration of about 15%. Thus, it is reasonable to expect severe localization effects in  $\alpha'$ - $\text{NaV}_2\text{O}_5$ , and the formation of a large-polaron if the electron–lattice interaction is sufficiently long-ranged.

The absorption coefficient for the photoionization of two-dimensional large polaron in adiabatic limit is [20],

$$\alpha \sim \frac{(kR)^2}{[1 + kR]^2} \quad (1)$$

where  $R$  is a confinement radius, and  $k = \sqrt{2m(\hbar\omega - 3E_b)}/\hbar$  is a free electron wave vector. The calculated absorption spectra of a large polaron in  $\alpha'$ - $\text{NaV}_2\text{O}_5$  are shown in Fig. 3. The photoionization begins when the photon energy exceeds three times the large polaron binding energy  $E_b$ . The spectra are clearly assymmetric, and in excellent agreement with measured ones, Fig. 3. Under doping, the shift of the absorption peak towards higher energies can be understood as a consequence of large-polaron size reduction together with a increase of the binding energy. Dominant effect is the increase of a binding energy, which is evident from the energy shift of a spectral threshold. It is important to note that peak due to



**Fig. 3.** Measured (lower panel) and calculated (upper panel) optical conductivity of  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  for  $E \parallel a$  polarizations.

photoionization of a large polaron is not observed in  $\sigma_b$  spectra in a nominally pure  $\alpha'$ - $\text{NaV}_2\text{O}_5$ . The reason for this could be existence of large inter-site Coulomb interaction e.g. large on-site Hubbard repulsion parameter  $U$ . Thus the optical properties along the  $b$ -axis are well described with modified Heitler-London model [7]. Upon doping the Hubbard repulsion is reduced and photoionization process becomes permissible. We believe that the peak at about 0.44 eV in  $\sigma_b$  originates from this effect. Electronic properties of  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  (at least up to concentrations that do not alter  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  crystal structure) still remain to be governed by ionic interactions and material never enters the metallic phase.

#### 4. CONCLUSION

In conclusion, we present the analysis of the optical properties of  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  using ellipsometric, and infrared reflectivity techniques. Despite strong hole-doping the material remains insulating up to the doping concentration of about 15%. The insulating state appears as a consequence of strong ionic bonding between sodium ions and V—O planes. The optical absorption peak at 0.9 eV is described as photoionization energy of a large polaron.

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