Charge ordering and optical transitions of LiV$_2$O$_5$ and NaV$_2$O$_5$

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Abstract

We present measurements of the polarized optical spectra of NaV$_2$O$_5$ and LiV$_2$O$_5$. In an energy range from 0.5 to 5.5 eV, we observe similar peaks in the $E \parallel a$ spectra of NaV$_2$O$_5$ and LiV$_2$O$_5$, which suggests similar electronic structures along the $a$ axis in both materials. On the other hand, we find an almost complete suppression of the peaks in $\sigma_b$ of LiV$_2$O$_5$ around 1 and 5 eV. We attribute this suppression to the charge localization effect originating from the existence of a double-chain charge-ordering pattern in LiV$_2$O$_5$.

PACS: 78.40.-q, 71.35.-y, 75.50.-y

In the past several years, quantum phenomena resulting from the low dimensionality of effective electron interactions in solids have been investigated with increasing intensity from both experimental and theoretical points of view. The increase in interest was partially motivated by the discovery of inorganic materials which exhibit quantum effects, such as the Sr–Cu–O system [1] or CuGeO$_3$ [2], and by a common belief that these studies would give us a better understanding of electron correlations in general.

The vanadate family of AV$_2$O$_5$ oxides have demonstrated a variety of the low-dimensional phenomena which originate from their peculiar crystal structures [3]. These oxides are quasi two-dimensional (2D) materials with layers formed by VO$_5$ square pyramids. The A atoms are situated between layers as intercalants, but in fact they determine the valence state of vanadium atoms (acting as charge reservoirs). If the A atoms belong to the first column in the periodic table, such as A = Li, Na, each valence electron is shared between two vanadium atoms. As a result the V ions are in a mixed valence-state with an average valence of +4.5. The common consequence of mixed valence in these structures is the appearance of a quasi-1D magnetic interaction, since chains carrying the spin (made of V$^{4+}$, S=1/2) are separated from each other by nonmagnetic chains (V$^{5+}$). In both LiV$_2$O$_5$ and NaV$_2$O$_5$ the 1D character of the magnetic ordering was confirmed [4, 5]. In addition, there is a possibility of the existence of strong valence fluctuations, and eventually charge ordering (CO) effects.
A very interesting interplay between spin and charge dynamics results in the phase transition discovered in NaV$_2$O$_5$ [4]. Up to now, accumulated experimental data [4,6–9] suggested that NaV$_2$O$_5$ exhibits the CO phase transition at $T=34$ K into a gapped spin-liquid ground state. The arguments are mostly based on the insensitivity of the phase-transition effects associated with magnetic fields. Subsequently, several theoretical analyses of the role of the electron correlations (intersite Coulomb interaction) in charge dynamics and/or charge ordering of NaV$_2$O$_5$ were presented [10–13]. In these studies, the various charge-ordering ground states were proposed for the low-temperature phase of NaV$_2$O$_5$. These concepts were tested by comparison with optical conductivity data [14–17] with some success but no consistent picture has yet emerged. None of the models proposed to date have reproduced optical transitions in the 0.8-5.5 eV range and provided an explanation for the origin of the low-frequency excitations (observed in both IR and Raman spectra) [14–17]. In fact, the central issue refers to the energy scale at which the CO in NaV$_2$O$_5$ should manifest itself, and what should be a fingerprint of it in the optical spectra.

In LiV$_2$O$_5$ the effects caused by the uniform vanadium valence are not observed [18], and the structure is assumed to be in a charge-ordered phase (without a spin gap) even at room temperature [19]. We have measured and compared the optical spectra of LiV$_2$O$_5$ and NaV$_2$O$_5$. On the basis of these results, we discuss the origin of optical excitations and CO ground states in both compounds, and the nature of the CO phase transition in NaV$_2$O$_5$.

Single crystals, with dimensions typically 1x3x0.2 mm (Na$_x$V$_2$O$_5$) and 2x3x1 (LiV$_2$O$_5$) along a, b, and c axes respectively, prepared as described in Ref. [20] were studied. The measurements were performed on (001) surfaces. Measurements of the polarized infrared reflectivity spectra were performed on Fourier transform spectrometer Bruker IFS 113V, in an energy range from 40 to 11000 cm$^{-1}$. An in situ overcoating technique was used in reflectivity measurement [21]. The reflectivity in the range from 1100 to 3300 cm$^{-1}$ was measured on an Atago Multiviewer spectrometer with multichannel detection system combined with a SPECTRA TECH IR-Plan microscope. A rotating-analyzer ellipsometer was used to measure the pseudodielectric function in 1.2-5.5 eV energy range.

At room temperatures the $\alpha'$-NaV$_2$O$_5$ and $\gamma$-LiV$_2$O$_5$ have orthorhombic unit cells [4,22] (described with space groups $Pmmm$, and $Pnma$, respectively), and crystal structures consisting of layers of VO$_5$ square pyramids which are mutually connected via common edges and corners making the characteristic V "zigzag" chains along the b axis. Parameters a and b, are similar in both compounds [4,22]. The c axis of LiV$_2$O$_5$ is approximately twice as large, since the LiV$_2$O$_5$ unit cell comprises four formula units (two in NaV$_2$O$_5$). In NaV$_2$O$_5$ all vanadium atoms are in uniform valence state at room temperatures (an average valence of +4.5), and thus indistinguishable in the unit cell (i.e. they occupy sites with same symmetry).

Conversely, the structure of LiV$_2$O$_5$ is characterized by two kinds of vanadium chains along the b axis. One is magnetic, V$^{4+}$ ($S=1/2$) and the other nonmagnetic V$^{5+}$ ($S=0$), see Fig.1. Another important difference in crystal structures comes from the different sizes of Li and Na ions. Li atoms are smaller, and consequently the VO layers in LiV$_2$O$_5$ are more corrugated, see Fig.1. An alternative description of the VO$_5$ layer is that it consists of V-O-V rungs coupled together in a ladder fashion through the oxygen bonds along the b
axis. These ladders are mutually connected to each other via a direct overlap of vanadium d orbitals along the $V^1_R - V^2_L - V^1_R$ "zigzag" chain, see Fig.1.

The optical conductivity of NaV$_2$O$_5$ and LiV$_2$O$_5$ is presented in Fig.2. The optical conductivity is calculated from the reflectivity data using Kramer-Kronig relations. The pseudodielectric functions of NaV$_2$O$_5$ and LiV$_2$O$_5$ are shown in Fig.3 The 1.5-5.5 eV energy range is computed using the ellipsometric equations for the isotropic case. Consequently, $\epsilon (\sigma)$ represents a complicated average of the projections of the dielectric tensor on the sample surface. We present the spectra of the (001) surface taken with the a axis (thin line) and the b axis (thick line) in the plane of incidence. Following Aspnes’s prescription, we attribute these components to the dielectric tensor components $\epsilon^2_{aa} (\sigma_a)$ and $\epsilon^2_{bb} (\sigma_b)$, respectively.

Bands with energies at 0.9, 1.2, 3.22, 4.23, and 5 eV for $\sigma_a$ and 1.1, 1.58, 3.73, and 5 eV for $\sigma_b$ are found in NaV$_2$O$_5$; see Fig. 2a. The same structures were observed in previous studies [14–17] as well. In LiV$_2$O$_5$ we find bands with energies centered at 0.85, 3.03, 4.20, and 4.95 eV for $\sigma_a$ and at 3.42 eV for $\sigma_b$. It is important to note that while $\sigma_a$ in LiV$_2$O$_5$ closely resembles $\sigma_a$ in NaV$_2$O$_5$, $\sigma_b$ in LiV$_2$O$_5$ is almost completely suppressed except 3.42 eV mode.

We first focus on excitations around 1 eV in the NaV$_2$O$_5$ spectra, and discuss the results in light of the electronic band structure of NaV$_2$O$_5$ obtained from density-functional calculations, (DFC’s) [25] and t-J-V model [10–13]. According to DFC’s, the vanadium d-level degeneracy is removed due to anisotropy of the crystal field [25] and the lowest occupied 3d$_{xy}$ states are separated by 1-5 eV from remaining 3d states. This energy scale provoked the assignment of 0.9 eV peak in the optical spectra, Fig.2, as a transition between d-d crystal-field levels of vanadium ions [15]. However, recent work on Ca-doped NaV$_2$O$_5$ showed that 0.9 eV peak decreases in intensity with increasing Ca, [26] This result seems to be inconsistent with the d-d transition picture (the d-d transition intensity should be proportional to the number of V$^{4+}$ ions). On the other hand, in the t-J-V model, the combined effects of the short-range Coulomb interaction and valence fluctuations of V ions determine the peak energies in the optical conductivity spectra, e.g. the anisotropy of the interband transitions in the a and b directions. In order to reproduce experimental observations, basically all t-J-V calculations rely on (or predict) the existence of strong charge discomensuration, which is not in accordance with effects related to the uniform valence in NaV$_2$O$_5$.

In fact, the quarter-filled nature of the V-O-V rung [23] (0.5 electrons per vanadium site) suggests that the band states are superposition of the $d_{xy}$ molecular orbitals of bonding and antibonding types. Then it can argued that 0.9 eV structure corresponds to the bonding-antibonding transition within the V-O-V rung [14]. The energy separation of the bonding-antibonding $d_{xy}$ orbitals, according to the Hubbard model of the isolated rung, is $\Delta E_{BA} \sim 2t_a$. A reasonable value of $t_a = 0.45$ eV reproduces the energy band at 0.9 eV in $E \parallel a$ spectra. Such an analysis predicts the existence of a similar structure along the b-direction as indeed observed in the 1.2 eV peak in $\sigma_b$.

The temperature dependence of the optical conductivity raises even more questions. All the features in $\sigma_a$ spectra increase in intensity, but without a change of energy at CO phase transition temperature, $T_c = 34K$, [16,27]. According to the t-J-V model, strong energy dependence of 0.9 eV structure is expected across the phase-transition temperature, since the driving mechanism for the CO is short-range Coulomb interaction (which induces a non
zero in-rung charge disproportion potential [11,14]). Switched on at $T_c$, this interaction naturally produces “zigzag” charge order. Thus one may either conclude that change of charge disproportion below phase transition is very small [27] [this contrasts with the strong splitting of V NMR lines observed below $T_c$ (Ref.7)] or that CO does not manifests itself through the change of energy of 0.9 eV peak.

With this in mind, let us now discuss the optical conductivity of LiV$_2$O$_5$. If we assume the bonding-antibonding transition (with and/or without the charge disproportion potential $\Delta$) to be responsible for the 0.9 eV optical excitation in $\sigma_a$ spectra of NaV$_2$O$_5$, the existence of a similar structure (0.85 eV) in LiV$_2$O$_5$ at first seems to be completely unexpected. The reason for this is the existence of plane corrugation and strong double chain charge ordering in LiV$_2$O$_5$. However, despite corrugation, the $3d_{xy}$-$2p-3d_{xy}$ bonds of the rungs in these two compounds are similar. According to the crystal structures, the V-O-V bond angles differ in these two structures by $10^\circ - 20^\circ (120^\circ$ in LiV$_2$O$_5$ and $140^\circ$ in NaV$_2$O$_5$); see Fig.1. Such a structural difference would eventually cause a somewhat smaller $t_a$ hopping in LiV$_2$O$_5$. If we discard $\Delta$, we find $t_a \sim 0.42\text{eV}$ in LiV$_2$O$_5$. On the other hand, the double-chain charge order in LiV$_2$O$_5$ should give completely different $\Delta$ then in NaV$_2$O$_5$, which should cause large difference in the optical conductivity, which is not observed. So, whether or not the difference in charge disproportion between these compounds manifests itself in $E || a$ peak energies is still an open question.

Intensity estimates are much more difficult to perform. In the simplest approach, the changes in intensity are produced by different hoppings. In NaV$_2$O$_5$ the $E || a$ peak is around three times more intense than the $E || b$ peak. Thus, according to the t-J-V model [13], the hopping energy $t_b$ is expected to be at least two times smaller, $t_b \sim 0.2 \text{eV}$. From LiV$_2$O$_5$ optical spectra we learned that major effect of charge localization involves peak intensities. As we already discussed, LiV$_2$O$_5$ is at room temperature in a charge-ordered state, i.e. a double-chain charge ordering of electrons along the b axis, see Fig.1. In this case the electronic transitions along b axis to a states with double-site occupancies should be almost completely suppressed. This is evident by vanishing of the structures around 1 eV in $E || b$ spectra of LiV$_2$O$_5$. This effect is caused by a reduced probability for the electrons to hope along the b axis or in the xy direction that are already occupied. This is consistent with the vanishing of the structures around 1 eV in the $\sigma_b$ spectra of LiV$_2$O$_5$.

The $E || a$ bonding-antibonding transition is not influenced by the double-chain charge ordering pattern in LiV$_2$O$_5$ as much as processes described above, and we still find the peak at 0.85 eV. Its intensity is approximately two times smaller than the 0.9 eV peak in NaV$_2$O$_5$, indicating that charge-localization also affect (in some way) this process. If so, suppression of the 0.9 eV peak in NaV$_2$O$_5$ is expected below the phase transition and indeed observed in Ref. 27.

Therefore, the intensities of the peaks along the b axis in the optical conductivity of NaV$_2$O$_5$ should be strongly temperature dependent if the CO below $T_c$ is of ”in-line” type. This is not observed in the experiment, firmly establishing the ”zigzag” CO scenario in NaV$_2$O$_5$, [11].

Keeping in mind the complete disappearance of the 1.1 and 1.6 eV peaks in the $\sigma_b$ spectra of LiV$_2$O$_5$, we propose that these two structures in NaV$_2$O$_5$ originate from electronic transitions which involve double-electron occupation of the rungs created in neighboring ladders or the same ladder, respectively; see Fig.1. That is, the $E || b$ experimental configuration
allows both intraladder and interladder transitions, while the $E \parallel a$ configuration allows only interladder transitions. Thus the interladder transitions could correspond to 1.1 eV peak (Fig. 2), which has a similar intensity in both $\sigma_a$ and $\sigma_b$ spectra. Different energies of intraladder and interladder transitions could be related to the Coulomb potential difference in the following way: Let us assume that double-electron occupancy costs an effective energy $V$ for the isolated rung. Then the total potential difference between these two cases is (taking $V_{xy} \sim \sqrt{2}V$) $\Delta E = (2V + 2V_{xy}) - (3V + V_{xy}) = \sim 0.4V$. Taking $V=1$ eV, we obtain $\Delta E \sim 0.4$eV. Since experiment gives an energy difference of about 0.5 eV, the additional energy difference between of about 0.1 eV could be due to the difference in hopping. If so, the first consequence is that interladder hopping $t_{xy}$ is not an order of magnitude smaller than $t_b = 0.23$ eV ($J_b = 4t_b^2/U$ $J \sim 560K$), but rather just factor of two or three smaller, $t_{xy} \sim 0.1eV$. Such a conclusion is consistent with previous estimates [28] and with arguments involving magnetic dimer formation along the xy direction, which follows from the "zigzag" charge-ordered ground state [10].

The structures around 3-4 eV do not show much difference in these two compounds. According to the angle-resolved photoemission spectroscopy results [24], we assign 3.22 and 3.73 eV peaks to $O_{2p} - V_{3d}$ transitions within the same V-O-V rungs.

In conclusion, we studied the electronic properties of NaV$_2$O$_5$ and LiV$_2$O$_5$ by measuring the optical reflectivity and dielectric functions of these two compounds in the 0.5 - 5.5 eV energy range. While $\sigma_a$ is similar in both compounds the $\sigma_b$ is strongly suppressed around 1 and 5 eV in LiV$_2$O$_5$. We attribute this effect to charge-localization originating from the double in-line charge-ordering pattern in LiV$_2$O$_5$. Our results, thus, support the zigzag charge-ordering ground state in NaV$_2$O$_5$ below the phase-transition temperature.

Acknowledgement: This work was supported by the Natural Sciences and Engineering Research Council of Canada, and Simon Fraser University. * mkonstan@sfu.ca
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FIGURES

FIG. 1. Schematic representation of the (a) LiV$_2$O$_5$ and (b) NaV$_2$O$_5$ crystal structures.

FIG. 2. Room temperature optical conductivity of NaV$_2$O$_5$ and LiV$_2$O$_5$.

FIG. 3. Imaginary part of the pseudodielectric function of NaV$_2$O$_5$ and LiV$_2$O$_5$. 
Konstantinovic et al. Fig. 1

- **O**
- **V**
- **Li, Na**
- **V$_{3d}$ electron**

Diagram showing the crystal structure of:
- **LiV$_2$O$_5$**
- **NaV$_2$O$_5$**

Key:
- $V^{4+}$
- $V^{5+}$
- $V_L^2$
- $V_R^1$
- $V_{4.5+}$
- $V_{xy}$

Legend:
- Black dots: O
- Purple dots: V
- Green dots: Li, Na
- Red diamonds: V$_{3d}$ electron
Konstantinovic et al. Fig. 2

Graph showing the conductivity ($\sigma$) of $\text{LiV}_2\text{O}_5$ and $\text{NaV}_2\text{O}_5$ as a function of energy (eV). The conductivity is given in units of $(\Omega^{-1} \text{ cm}^{-1})$. Two curves are plotted, labeled $\sigma_a$ and $\sigma_b$. The graph shows a peak for $\text{LiV}_2\text{O}_5$ at around 1.5 eV and a peak for $\text{NaV}_2\text{O}_5$ at around 2.5 eV.
