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

M. J. Konstantinović,* J. Dong, M. E. Ziaei, B. P. Clayman, and J. C. Irwin

Simon Fraser University, Physics Department, 8888 University drive, Burnaby, British Columbia, V5A1S6 Canada

K. Yakushi

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

M. Isobe and Y. Ueda

Institute for Solid State Physics, The University of Tokio, 7-22-1 Roppongi, Minato-ku, Tokio 106, Japan

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 $E\|a$ 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 σ_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$_5$.

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 that exhibit quantum effects, such as the Sr-Cu-O system[1] or CuGeO$_3$,[2] and by a common belief that these studies will give us a better understanding of electron correlations in general.

The vanadate family of AV_2O_5 oxides have demonstrated a variety of 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 and 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 a CO phase transition at T = 34 K into a gapped spin-liquid ground state. The arguments in favor of CO are mostly based on the insensitivity of the phase-transition effects associated with magnetic fields (the spin-Peierls phase transition scenario was also proposed). Subsequently, several theoretical analyses of the role of the electron correlations (intersite Coulomb interaction) in charge dynamics and/or charge ordering in NaV$_2$O$_5$ were presented.[10–13] In these studies, various charge-ordering ground states were proposed for the low-temperature phase of NaV$_2$O$_5$. These models 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-eV, range and provided an explanation for the origin of the low-frequency electronic excitations (observed in both IR and Raman spectra).[14,9] 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 $1 \times 3 \times 0.2$ mm^3 (Na$_x$V$_2$O$_5$) and $2 \times 3 \times 1$ (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 a 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 α'-NaV$_2$O$_5$ and γ-LiV$_2$O$_5$ have orthorhombic unit cells[6,22] (described by the space groups $Pmmn$ and $Pnma$, respectively), and crystal structures consisting of layers of VO$_5$ square pyramids which are mutually connected via common edges and corners making
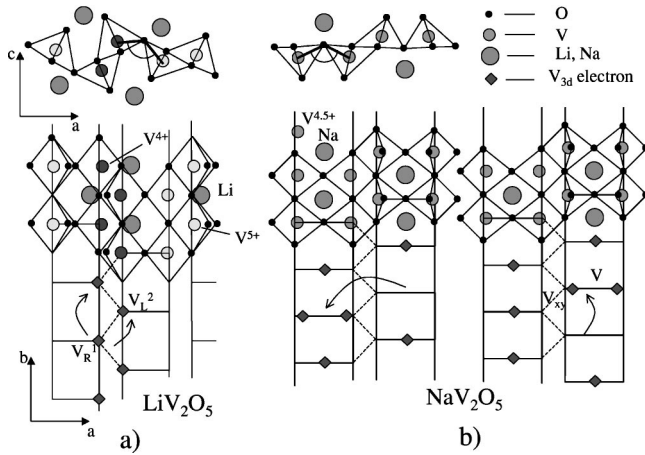
FIG. 1. Schematic representation of the (a) LiV_2O_5 and (b) NaV_2O_5 crystal structures.

characteristic ''zigzag'' chains of V atoms along the b axis. Parameters a and b are similar in both compounds.[6,22] The c axis of LiV_2O_5 is approximately twice as large, since the LiV_2O_5 unit cell comprises four formula units (two in NaV_2O_5). In NaV_2O_5 all vanadium atoms are in the same valence state at room temperatures (an average valence of $+4.5$), and thus indistinguishable in the unit cell.

Conversely, the structure of LiV_2O_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_2O_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_R^1-V_L^2-V_R^1 ''zigzag'' chain; see Fig. 1.

The optical conductivity of NaV_2O_5 and LiV_2O_5 is presented in Fig. 2. The optical conductivity was calculated from the reflectivity data using Kramer-Kronig relations. The pseudodieletric functions of NaV_2O_5 and LiV_2O_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,[23] we attribute these components to the dielectric tensor components ϵ_{aa}^2 (σ_a) and ϵ_{bb}^2 (σ_b), respectively.

Bands with energies at 0.9, 1.2, 3.22, 4.23, and 5 eV for σ_a and 1.1, 1.58, 3.73, and 5 eV for σ_b are found in NaV_2O_5; Fig. 2. The same structures were observed in previous studies[14–17] as well. In LiV_2O_5 we find bands with energies centered at 0.85, 3.03, 4.20, and 4.95 eV for σ_a and at 3.42 eV for σ_b. It is important to note that while σ_a in LiV_2O_5 closely resembles σ_a in NaV_2O_5, σ_b in LiV_2O_5 is almost completely suppressed except for the 3.42-eV mode.
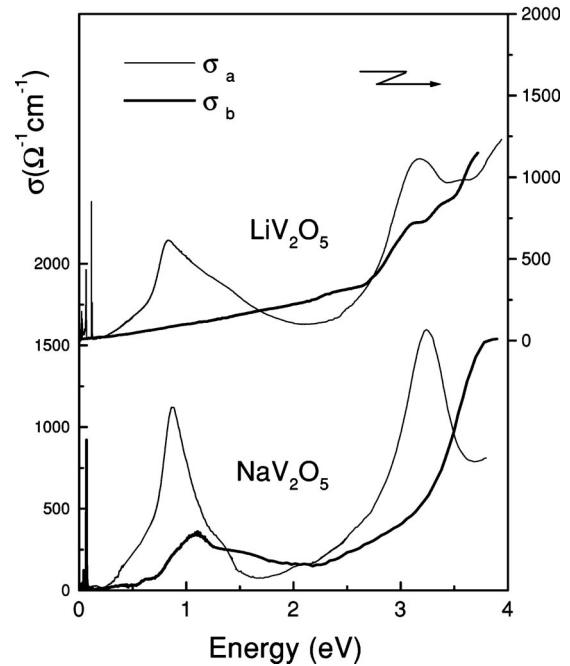

FIG. 2. Room temperature optical conductivity of NaV_2O_5 and LiV_2O_5.

We first focus on excitations around 1 eV in the NaV_2O_5 spectra, and discuss the results in light of the electronic band structure of NaV_2O_5 obtained from density-functional calculations (DFC's)[25] and a 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 the
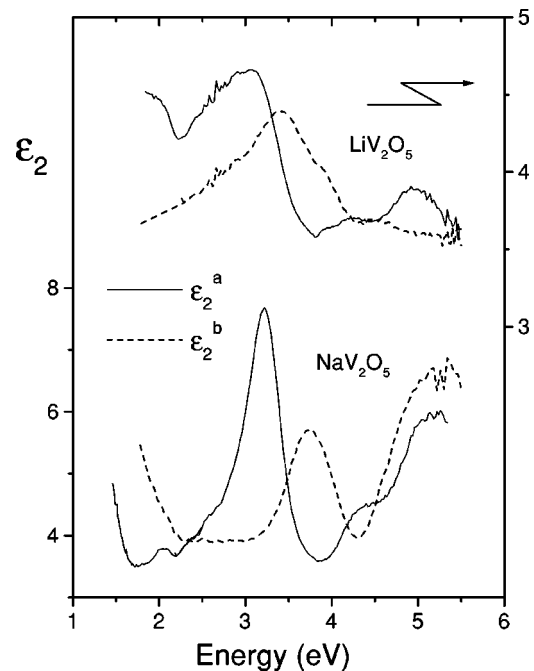

FIG. 3. Imaginary part of the pseudodielectric function of NaV_2O_5 and LiV_2O_5.

0.9-eV peak in the optical spectra (Fig. 2) to a transition between d-d crystal-field levels of vanadium ions.[15] However, recent work on Ca-doped NaV$_2$O$_5$ showed 0.9-eV 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 the V ions determines 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 discommensuration, 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[25](0.5 electrons per vanadium site) suggests that the band states are a superposition of the d_{xy} molecular orbitals of bonding and antibonding types. Then it can be argued that the 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 $E \| a$ 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 σ_b.

The temperature dependence of the optical conductivity raises even more questions. All the features in σ_a increase in intensity, but without a change of energy at the CO phase transition temperature, $T_c = 34$ K.[16,27] According to the t-j-V model, the energy shift of the 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 nonzero 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 the change of charge disproportion below the 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 manifest itself through a change in 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 Δ) to be responsible for the 0.9-eV optical excitation in σ_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 $10°$–$20°$ ($120°$ in LiV$_2$O$_5$ and $140°$ 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 Δ, we find $t_a \sim 0.42$ eV in LiV$_2$O$_5$. On the other hand, the double-chain charge order in LiV$_2$O$_5$ should

give a completely different Δ then in NaV$_2$O$_5$, which in turn should produce a 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 the $E \| a$ peak energies is still an open question.

Intensity estimates are much more difficult to obtain. In the simplest approach, changes in the 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, $t_b \sim 0.2$ eV. From the LiV$_2$O$_5$ optical spectra we learned that the major plausible effect of charge localization involves changes in peak intensities. As we already discussed, the 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 that involve double-site occupancies along the b axis should be almost completely suppressed. This effect is caused by a reduced probability for the electrons to hop to sites 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 σ_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 the 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 might also affect this process in some way. 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$_5$.[10]

Keeping in mind the complete disappearance of the 1.1- and 1.6-eV peaks in the σ_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 $E \| a$ configuration allows only interladder transitions. Thus the interladder transitions could correspond to the 1.1-eV peak (Fig. 2), which has a similar intensity in both σ_a and σ_b spectra. Different energies for the 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 of about ~ 0.1 eV could be due to the difference in hopping. If so, the first consequence is that interladder hopping $t_{xy} \sim 0.1$ eV is just a factor of 2 or 3 smaller than $t_b = 0.23$ eV ($J_b = 4t_b^2/U$

$\sim$560 K).[5] Such a conclusion is consistent with a previous estimate[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 are quite similar in these two compounds. According to the angle-resolved photoemissions spectroscopy,[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_2O_5 and LiV_2O_5 by measuring the optical reflectivity and dielectric functions of these two compounds in the 0.5–5.5-eV energy range. While σ_a is similar in both compounds, σ_b is strongly suppressed around 1 and 5 eV in LiV_2O_5. We attribute this effect to charge localization originating from the double in-line charge-ordering pattern in LiV_2O_5. Our results thus support the zigzag charge-ordering ground state proposed for NaV_2O_5 below the phase-transition temperature.

*Email address: mkonstan@sfu.ca

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