

Low-temperature ellipsometry of α' - NaV_2O_5

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The dielectric function of α' - NaV_2O_5 was measured with electric field along the a and b axes in the photon-energy range 0.8–4.5 eV for temperatures down to 4 K. We observe a pronounced decrease of the intensity of the 1-eV peak upon increasing temperature with an activation energy of about 25 meV, indicating that a finite fraction of the rungs becomes occupied with two electrons while others are emptied as temperature increases. No appreciable shifts of peaks were found showing that the change in the valence state of individual V atoms at the phase transition is very small. A remarkable inflection of this temperature dependence at the phase transition at 34 K indicates that charge ordering is associated with the low-temperature phase.

α' - NaV_2O_5 is the subject of intensive research as a result of its remarkable physical properties. The compounds $A\text{V}_2\text{O}_5$ ($A = \text{Li}, \text{Na}, \text{Ca}, \text{Mg}, \text{etc.}$)¹ all have the same lattice structure, similar to that of V_2O_5 . The structure can be described as two-legged ladders with VO_5 pyramids forming the corners arranged in two-dimensional sheets. In $A\text{V}_2\text{O}_5$ the A atoms enter the space between the layers and act as electron donors for the V_2O_5 layers. In α' - NaV_2O_5 the average valence of the V ions corresponds to $\text{V}^{+4.5}$. X-ray diffraction indicates that at room temperature all V ions are crystallographically equivalent.^{2–4} At 35 K a phase transition occurs, below which the following changes take place: (i) A quadrupling of the unit cell,⁵ and (ii) the opening of a spin gap.⁵ In addition, there are several experimental hints for a charge redistribution below the phase transition, e.g., unaccounted for changes in entropy,⁶ splitting of the V-NMR lines,⁷ inequivalent V sites observed with synchrotron radiation x-ray diffraction.⁸ In this paper we investigate the charge redistribution using optical spectroscopic ellipsometry as a function of temperature. In our spectra we observe a clear indication of a strong charge redistribution between the rungs of the ladders at elevated temperature, which at the same time provides a channel for electrical conductivity with an activation energy of about 25 meV. We also report a remarkable inflection of the temperature dependence at the phase transition, which we interpret as an inflection of the charge redistribution process due to a particular correlated electronic state in which the charge and spin degrees of freedom are frozen out simultaneously.

The crystal (sample CR8) with dimensions of approximately 2, 3, and 0.3 mm along the a , b , and c axes, respectively, was mounted in a UHV optical cryostat in order to prevent the formation of ice on the surface. The pressure was about 10^{-8} mbar at 300 K and reached 10^{-9} mbar at 4 K. We performed 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 Θ of

80° was used in all experiments. In Ref. 9 we describe the details of the procedure followed to obtain $\epsilon(\omega)$.

The room-temperature results are in general agreement with previous results^{10,11} using Kramers-Kronig analysis of reflectivity data. Along the a direction we observe a peak at 0.9 eV with a shoulder at 1.4 eV, a peak at 3.3 eV, and the slope of a peak above 4.2 eV, outside our spectral window. A similar blueshifted sequence is observed along the b direction. The 1-eV peak drops rather sharply and extrapolates to zero at 0.7 eV. However, weak absorption has been observed within the entire far and mid-infrared range.^{12,10} The strong optical absorption within the entire visible spectrum causes the characteristic black appearance of this material. Based on the doping dependence of the optical spectra of $\text{Na}_{1-x}\text{Ca}_x\text{VO}_5$ we established in Ref. 9 the assignments made in Refs. 4, 13 and 10, namely that the peak at around 1 eV along the a and b direction is due to transitions between linear combinations of V $3d_{xy}$ states of the two V ions forming the rungs.^{4,13,10} In Refs. 4 and 13 even and odd combinations were considered. The 0.9-eV peak in $\sigma_a(\omega)$ (peak A) would then correspond to the transition from V-V bonding to antibonding combinations on the same rung.¹⁰ In Ref. 10 this model was extended to allow lop-sided linear combinations of the same orbitals, so that the 0.9-eV peak then is a transition between left- and right-oriented linear combinations. The work presented in Ref. 9 definitely rules out the assignment of these peaks to crystal-field-type V $d-d$ transitions proposed in Refs. 11 and 14.

The 1.1-eV peak in $\sigma_b(\omega)$ (peak B) involves transitions between neighboring rungs along the ladder. As a result of the correlation gap in the density of states, the optically induced transfer of electrons between neighboring rungs results in a final state with one rung empty, and a neighboring rung doubly occupied, in other words, an electron hole pair consisting of a hole in the band below E_F , and an electron in the empty state above E_F . Note that the final-state wave function is qualitatively different from the on-rung bonding-

antibonding excitations considered above (peak A), even though the excitation energies are the same:⁹ it involves one rung with no electron, and a neighboring rung with one electron occupying each V atom. We associate the lower energy of peak A compared to peak B with the attractive electron-hole Coulomb interaction, favoring on-rung electron-hole pairs. Optical transitions having values below 2 eV were also seen in V_6O_{13} and VO_2 . In V_2O_5 they have very small intensities, and were attributed to defects.¹⁵ The peak at 3.3 eV in $\sigma_a(\omega)$ we could attribute to a transition from the $2p$ orbital of oxygen to the antibonding level within the same V_2O cluster.⁹

Let us now address the temperature dependence of the spectra. Perhaps most striking of all is the fact that the *peak positions* turn out to be temperature independent throughout the entire temperature range. This behavior should be contrasted with the remarkable splitting of the V-NMR lines in two components below the phase transition.⁷ It has been suggested⁴ that the T_c marks the transition from a high-temperature phase where every rung is occupied with an electron residing in a H_2^+ -type bonding orbital (formed by the two V $3d_{xy}$ orbitals), to a low-temperature phase, where the system is in a charge ordered state (e.g., the zigzag ordered state^{16,17} with an alternation of V^{4+} and V^{5+} states, or, as suggested in Refs. 8 and 18 with $\text{V}^{4+}/\text{V}^{5+}$ ladders and $\text{V}^{4.5+}/\text{V}^{4.5+}$ ladders alternating). In Refs. 10 and 19 estimates have been made of the potential-energy difference between the left- and right-hand V sites on the same rung, in order to reproduce the correct intensity and photon energy of the 1-eV peak along a , as well as producing a $\text{V}^{4.9+}/\text{V}^{4.1+}$ distribution between left and right. This turned out to be $\Delta = V_L - V_R \approx 0.8$ eV, with an effective hopping parameter $t_{\perp} \approx 0.4$ eV. To have $\text{V}^{4.5+}/\text{V}^{4.5+}$ above and $\text{V}^{4+}/\text{V}^{5+}$ below the phase transition requires that the potential-energy difference changes from $\Delta = 0.8$ eV below T_c to 0 at and above T_c . As a result the ‘‘1-eV peak’’ would shift from 0.89 to 0.8 eV in the temperature interval between 0 and 34 K, and would remain constant above T_c . The observed shift is less than 0.03 eV within the entire temperature interval, and less than 0.01 eV between 0 and 34 K. This suggests that the change in Δ (and consequently the charge of the V atoms) at the phase transition is very small. In fact, a change of Δ from 0.1 eV to 0 across T_c , compatible with the experimental results, would yield a change in the valence state from $\text{V}^{4.44+}/\text{V}^{4.56+}$ to $\text{V}^{4.5+}/\text{V}^{4.5+}$ between 0 and 34 K, which is an almost negligible effect. Thus we conclude that, irrespective of the possible charge configurations $\text{V}^{4.5+}/\text{V}^{4.5+}$ or $\text{V}^{5+}/\text{V}^{4+}$, the changes in the charges of the V atoms at the phase transitions are very small (smaller than $0.06e$).

As we can see in Figs. 1(b) and 2(b), there is a strong decrease of the *intensity* of the peaks A and B with the increase of the temperature. The spectral weight for both cases is not transferred to low frequencies.¹⁰ The spectral weight of the B peak seems to be recovered up to and above 4 eV. The spectral weight of the B peak in the a direction is recovered also in the nearby high frequencies,^{20,14} whereas the intensity of the A peak seems to be recovered at even higher photon energy, probably 4.5 eV.²⁰ The evolution of the 1-eV peaks can be seen from Fig. 3, where the integrated intensities in $\sigma_1(\omega)$ from 0.75 eV to 2.25 eV were plotted as a function of temperature. The data fitted with the formula

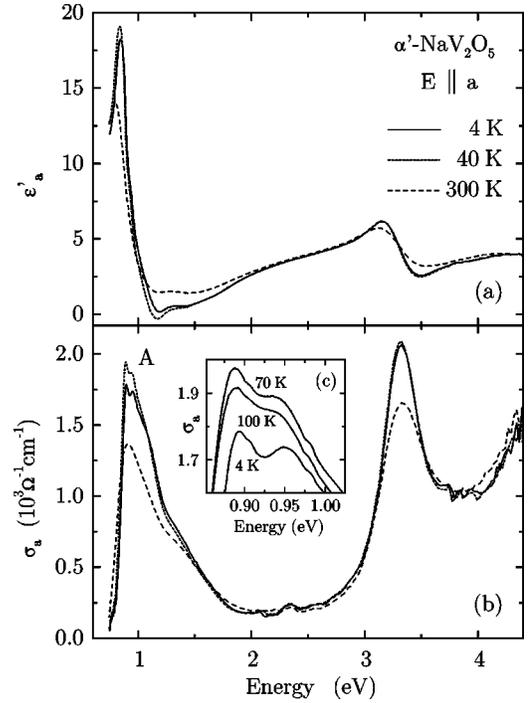


FIG. 1. Real part $\epsilon'(\omega)$ of the complex dielectric function (a) and optical conductivity $\sigma_1(\omega)$ (b) for $E||a$.

$I(T) = I_0(1 - f e^{-E_0/T})$ gave $f = 0.35$ and $E_0 = 286$ K for the a direction and $f = 0.47$ and $E_0 = 370$ K for the b direction. From the fits we see that the activation energy E_0 is about 25 meV, which is very small for the frequency range of the peaks. A decrease of the intensity of the A peak takes place below the phase transition, but otherwise there are no features related to it. The splitting of the A peak of about 55 meV [Fig. 1(c)] exists even at 100 K. Judging from its sharp

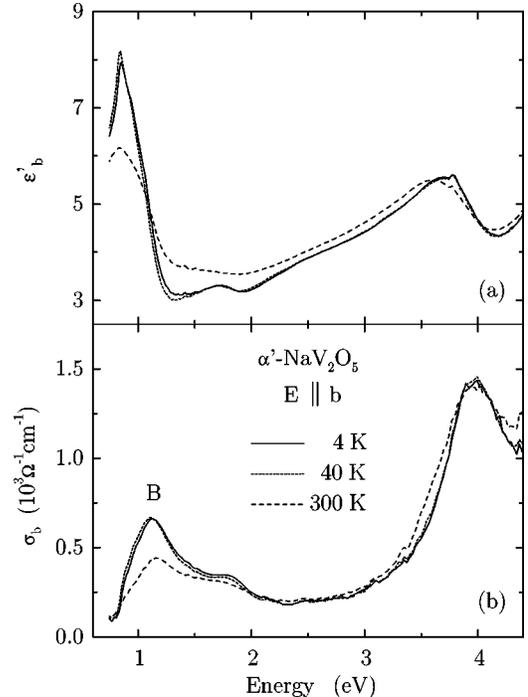


FIG. 2. Real part $\epsilon'(\omega)$ of the complex dielectric function (a) and optical conductivity $\sigma_1(\omega)$ (b) for $E||b$.

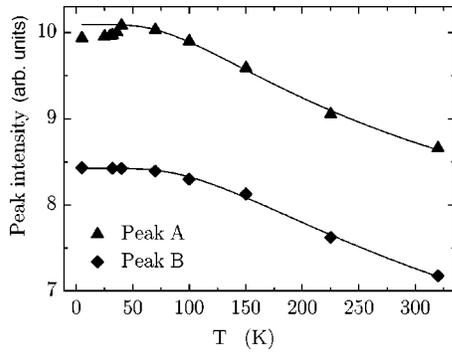


FIG. 3. Intensity of the 1-eV peaks detected along the a and b axes (peaks A and B, respectively), plotted vs temperature. Solid lines are fits to the formula $I(T) = I_0(1 - f e^{-E_0/T})$.

shape and the value of splitting, it can be attributed to a phonon sideband.

Band-structure calculations have indicated that the d_{xy} orbitals are well separated from the other d orbitals⁴ and ESR experiments have led to g values that indicate the complete quenching of the orbital momentum.²¹ There are then no other low-lying crystal field levels, about 25 meV above the ground state, to play a role in the temperature dependence behavior of the A peak. Comparing the doping dependence of the A peak in $\text{Ca}_x\text{Na}_{1-x}\text{V}_2\text{O}_5$ (Ref. 9) and the high-temperature dependence from Fig. 1(b) we see that the two behaviors resemble each other, presenting no shifting or splitting. But, as discussed in Ref. 9, the intensity of the A peak decreases upon doping because doping induces doubly occupied rungs. The same mechanism can then be responsible for the decrease of the intensity of the A peak with increasing temperature. The bonding-antibonding transition (A peak) on the rung will have a reduced intensity, as there are fewer singly occupied rungs, as in the case of $\text{Ca}_x\text{Na}_{1-x}\text{V}_2\text{O}_5$.⁹ The transitions on the doubly occupied rungs are at an energy U , around 4 eV, with a factor $4t_{\perp}/U$ reduction of the original spectral weight.⁹ The activation energy of 25 meV would then be the energy required to redistribute the electrons between the rungs, either on the same ladder, or between different ladders. Eventually, at very high temperatures, only half of the rungs would be occupied with one electron, so the intensity of the A peak would be at half the low-temperature value ($f=0.5$ in the fitting formula of Fig. 3).

At first glance the processes leading to partial emptying of rungs, while doubly occupying others, seem to be of the order of the energy of peak B (1 eV), which corresponds exactly to such a process and one may wonder how a low-energy scale could exist. However, processes involving the *collective* motion of charge can be at a much lower energy than the single-particle charge transfer, as a result of short-range (nearest-neighbor) Coulomb interactions. An example of such a collective mode is the zigzag ordering^{16,19} involving an (almost) soft charge mode for k at the Brillouin-zone (BZ) boundary. These *charge* modes, because k is at the BZ boundary, can appear only indirectly (e.g., phonon assisted) in $\sigma(\omega)$, and therefore are at best weakly infrared active. Under favorable conditions the *spin* degrees of freedom¹⁰ in addition result in a weak but finite $\sigma(\omega)$. Another way in which the electrons can move from one rung to another is by

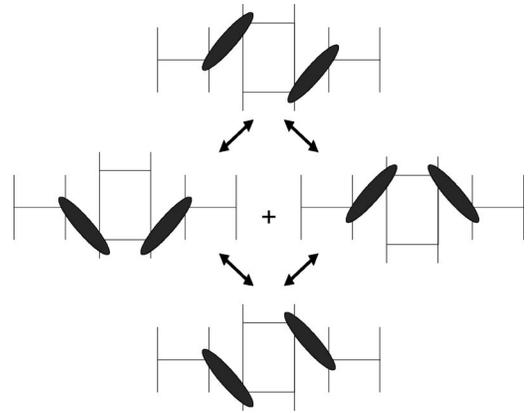


FIG. 4. The correlated electron state in the low-temperature phase is a superposition of the four configurations displayed in the figure.

forming topological defects, such as domain cells separating charge ordering domains. Macroscopically this could lead to double occupancy of some rungs and emptying others.

In fact, even though the optical gap is 1 eV, there are experiments which indicate charge degrees of freedom at a much lower energy. Resistivity measurements yielded an energy gap ranging from 30 meV at lower temperatures to 75 meV at high temperatures.²² The dielectric loss ϵ'' for frequency of 16.5 GHz along the b direction is rather constant up to 150 K and then increases very rapidly above 200 K (Ref. 23) (so that the microwave signal is lost at room temperature), meaning that an absorption peak could start to evolve at 200 K for very low frequencies. A low-frequency continuum was observed near 25 meV with infrared spectroscopy¹⁰ and at 75 meV with Raman spectroscopy.¹¹ Also infrared measurements¹⁰ found that $\sigma_{1,a}$ increases with increasing temperature.

The suppression of intensity below the phase transition in this context (Fig. 3) seems to mark a redistribution of charge which is associated with the spin gap. X-ray diffraction indicates that the superstructure below T_c consists of a group of four rungs:¹⁸ two neighboring rungs of the central ladder, one on the left-hand and one on the right-hand ladder. The presence of a spin-gap indicates that the four spins of this structural unit form an $S=0$ state below T_c . To account for the absence of a change of the valence of the V atoms at the phase transition, as well as for the slight double occupancy below the phase transition, the following scenario can be put forward. Below T_c the structure would be formed by singlets (see Fig. 4). A possible arrangement, which is motivated by the observed crystal structure at low temperature⁸ is indicated in Fig. 4. It corresponds to mainly two degenerate configurations involving one electron on each rung (top and bottom), engaged in a singlet formed of two electrons on nearest neighbor V positions on *different* ladders. These diagonal singlets were originally proposed by Chakraverty *et al.*²⁴ for $\text{Na}_{0.33}\text{V}_2\text{O}_5$. The middle two configurations are at higher-energy states of order 1 eV, hence they are only slightly mixed in. Because the latter configurations have one empty and one doubly occupied rung, the intensity of the A and B peak should again be reduced, as was discussed for temperatures above the phase transition. The reduced intensity in our spectra below T_c then reflects the amount of sin-

glet character involving doubly occupied rungs. Passing the phase transition the coherence of this state would vanish. This would result in a random configuration with an average valence of +4.5 for the V atoms, and also a spin susceptibility for the high-temperature phase due to the appearance of some free spins. The nature of the weak charge redistribution which we observe at low temperature would then be manifestly *quantum mechanical*.

In conclusion, we have measured the temperature dependence behavior of the dielectric function along the a and b axes of α' - NaV_2O_5 in the photon energy range 0.8–4.5 eV for temperatures down to 4 K. No appreciable shifts of the 1 eV peaks were found, thus showing that the change in the valence state of the V atoms at the phase transition is very small (smaller than $0.06e$). A strong decrease of the 1 eV peaks with increasing temperature was observed. We as-

signed this temperature dependence behavior to collective charge redistribution, namely the redistribution of the electrons among the rungs resulting in double occupation of some rungs as temperature increases, with an activation energy of about 25 meV. Below the phase transition, a small but sharp decrease of intensity of the 0.9-eV peak in $\sigma_a(\omega)$ was found. It was attributed to a finite probability of having, in the singlet state below T_c , configurations with electron pairs occupying the same rung.

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