# Charge-Ordering Signatures in the Optical Properties of $\beta$-$Na_{0.33}V_2O_5$

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Temperature dependent optical spectra are reported for $\beta$-$Na_{0.33}V_2O_5$. The sodium ordering transition at $T_{Na} = 240$ K and, in particular, the charge ordering transition at $T_{MI} = 136$ K strongly influence the optical spectra. The metal-insulator transition at $T_{MI}$ leads to the opening of a pseudogap ($\hbar\omega = 1700$ cm$^{-1}$) and to the appearance of a large number of optical phonons. These observations and the presence of a midinfrared band (typical for low dimensional metals) strongly suggest that the charge carriers in $\beta$-$Na_{0.33}V_2O_5$ are small polarons.

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Low dimensional metals feature a variety of metal-insulator (MI) transitions resulting from electron-phonon or electron-electron interactions. In charge density wave systems, such as $NbSe_3$ [1] and $K_{0.3}MoO_3$ [2,3], a MI transition is induced by a strong electron-phonon coupling (Peierls state). In $Fe_3O_4$ and $Ti_4O_7$ [4], which are polaronic materials, a MI transition is induced by small polaron ordering (Verwey state). Finally, in systems lacking sufficiently strong electron-phonon interaction, such as $(Me_2 - DCNQI)_2Li_{1-x}Cu_x$ [5,6], a MI transition may occur due to charge ordering resulting from electronic Coulomb interactions (Wigner crystal). Materials of which the properties are dominated by electron-phonon interaction often show the appearance in the insulating state of a large number of phonons in the infrared spectrum along the chain direction. This phenomenon, discussed by Rice *et al.* [7] for the 1D organic Peierls compound $TEA(TCNQ)_2$, has been found in several materials [1–3,8], including those showing a Verwey transition. One of the intriguing features of all these materials is that they show a so-called midinfrared band in the optical spectra. It has been argued that for $Fe_3O_4$ [9], and many other materials [10], the midinfrared band can be understood as a polaronic response. However, also materials where Hubbard physics dominates may show a relatively strong midinfrared band resulting from intraband transitions [5,6,11,12].

The recent discovery [13] of a clear metal-insulator transition (MIT) in the vanadium bronze $\beta$-$Na_{0.33}V_2O_5$ has sparked a revival of interest in this quasi-one-dimensional (1D) metallic system. The room temperature crystal structure [14] of $\beta$-$Na_xV_2O_5$ presents three crystallographically distinct vanadium sites, labeled $V_1$, $V_2$, and $V_3$. The Na atoms occupy lattice positions which can be represented as a ladder along the $b$ axis (the chain direction). For $x = 1/3$ only 50% of these lattice sites is occupied, each rung hosting one Na atom randomly distributed between the left- and right-hand sides of the ladder. Each Na atom donates one electron to the otherwise empty vanadium $d$ bands. It is believed [15] that these electrons are shared among the three V chains above the metal-insulator transition $T_{MI} = 136$ K, and that they condense on the $V_1$ zigzag chain or the $V_2$ ladder below $T_{MI}$. The metallic nature is rapidly lost for small deviations from $x = 0.33$ [13]. The presence of metallic behavior for only a sharply defined charge carrier concentration is different from conventional MIT in two or three dimensions, where the metallic phase occurs in a broad range of carrier densities above the critical value. This unusual doping dependence probably results from the potential created by the neighboring Na atoms. Doping away from $x = 1/3$ creates empty or fully occupied rungs on the Na ladder leading to large potential variations at the vanadium sites, and thus a decreased conductivity and eventually a localization of the charges.

$\beta$-$Na_{0.33}V_2O_5$ exhibits three phase transitions as a function of temperature: A sodium ordering transition at $T_{Na} \cong 240$ K accompanied by a doubling of the unit cell along $b$, a MI transition at $T_{MI} \cong 136$ K showing an additional tripling of the unit cell [16], and finally an antiferromagnetic transition at $T_{CAF} \cong 22$ K [13,17,18]. The nature of the MI transition in $\beta$-$Na_{0.33}V_2O_5$ is presently unclear. There has been a suggestion that it results from *bipolaronic* ordering [19,20]. But since the temperature dependent magnetic susceptibility [13] shows that the spins of the charge carriers remain unpaired in the insulating state this is an unlikely scenario. Another suggestion is that the charge ordering transition is a Peierls transition [21]. This, however, is based on the assumption that $\beta$-$Na_{0.33}V_2O_5$ becomes a quarter filled system below $T_{MI}$, which is contradicted by experiments showing a tripling of the unit cell along the $b$ direction. As is clear from the above, the origin of the MI transition as well as the nature of the charge carriers and the relevance of electron-phonon interactions remain open problems in $\beta$-$Na_{0.33}V_2O_5$. This motivated the present study on the temperature dependent optical conductivity of $\beta$-$Na_{0.33}V_2O_5$.

  

Single crystals have been prepared as described in [13]. We measured the reflectivity in the range 20–6000 $cm^{-1}$ as a function of temperature with a polarization both parallel and perpendicular to the $b$ direction (i.e., parallel to the conducting chains). Figure 1 shows the reflectivity spectra for some selected temperatures. In addition, we used spectroscopic ellipsometry to determine the dielectric function from 6000 to 36 000 $cm^{-1}$ at room temperature. The optical conductivity was obtained by combining the reflectivity and ellipsometry data and performing a Kramers-Kronig analysis (see Fig. 2). The one-dimensional nature of $\beta$-$Na_{0.33}V_2O_5$ is clearly reflected in the room temperature spectra. The $b$ direction shows a finite low frequency conductivity extrapolating to 200 $\Omega\,cm^{-1}$ at zero frequency. This value is somewhat better than the dc value of 100 $\Omega\,cm^{-1}$ measured previously [13]. In contrast, the conductivity in the perpendicular direction shows a typical insulating behavior in that the conductivity extrapolates to zero for zero frequency. The other features observed in the spectra are several relatively sharp phonon lines, and more importantly a relatively strong midinfrared band along the chain direction. The sodium ordering and, in particular, the MI transitions strongly influence the optical spectra. At the sodium ordering transition a small number of new phonon modes appear in the $E \perp b$ polarization. Their intensities have a slow temperature dependence reminiscent of an order/disorder transition and in good agreement with the temperature evolution of the satellites observed in x-ray diffraction experiments [22]. This is exemplified for a mode appearing at 990 $cm^{-1}$ in Fig. 3(b). More spectacularly, the MI transition results in the appearance of a large number of sharp phonon lines [more than 60 for the polarization along the $b$ direction; see Fig. 3(a) for a detailed view]. This evidences the presence of strong electron-phonon coupling in $\beta$-$Na_{0.33}V_2O_5$. Another indication for important electron-phonon interactions is the observation of strongly distorted phonon line shapes in the low frequency part ($< 150$ $cm^{-1}$) of the conductivity along the $b$ direction [Fig. 2(a)]. The temperature dependence of the intensity of the phonons appearing in the insulating state exhibits a clear second-order nature [see Fig. 3(b), 950 $cm^{-1}$ mode]. A second change in the optical conductivity below the MI transition is the opening of a pseudogap below 1700 $cm^{-1}$ in the $b$ direction [see Figs. 2(a) and 3(c)]. This opening of the pseudogap, apparent as a clear decrease in the background intensity below $T_{MI}$, is somewhat obscured by the appearance of the many phonon peaks in the insulating phase.

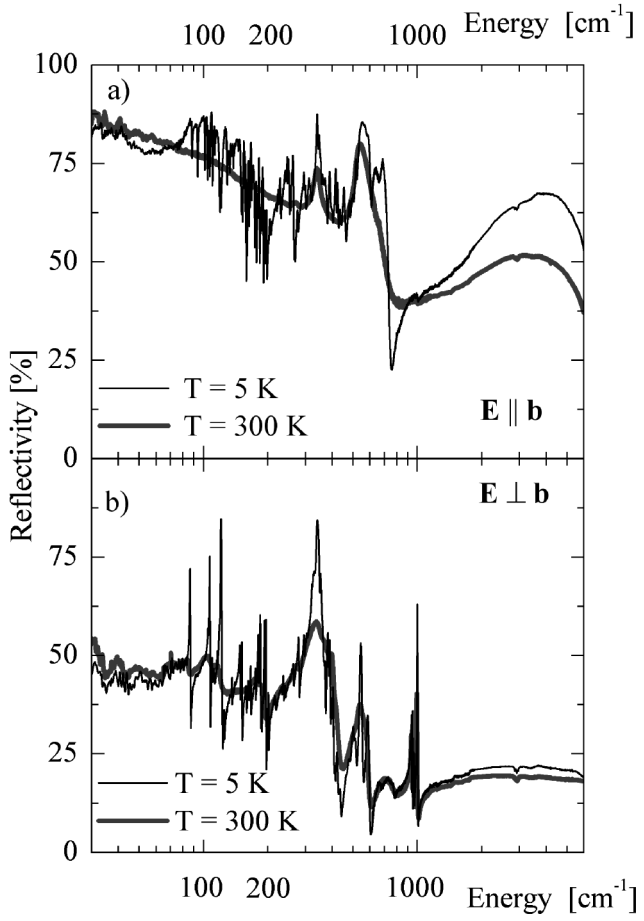


FIG. 1. Reflectivity spectra of $\beta$-$Na_{0.33}V_2O_5$ for $\mathbf{E} \parallel \mathbf{b}$ (a) and $\mathbf{E} \perp \mathbf{b}$ (b).

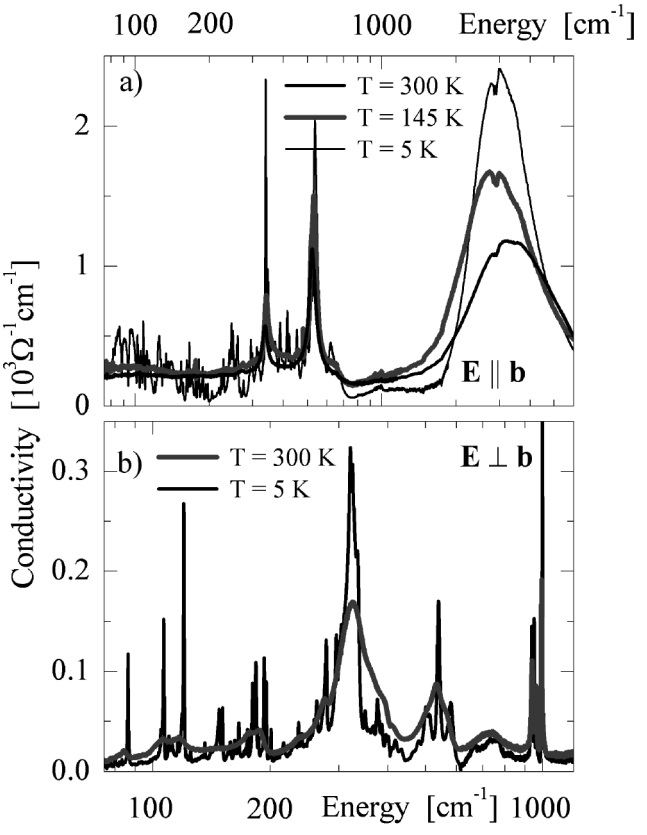


FIG. 2. The optical conductivity for $\mathbf{E} \parallel \mathbf{b}$ (a) and $\mathbf{E} \perp \mathbf{b}$ (b). The two small dips on the 3000 $cm^{-1}$peak are due to water absorption. Note the different energy scales in panels (a) and (b).

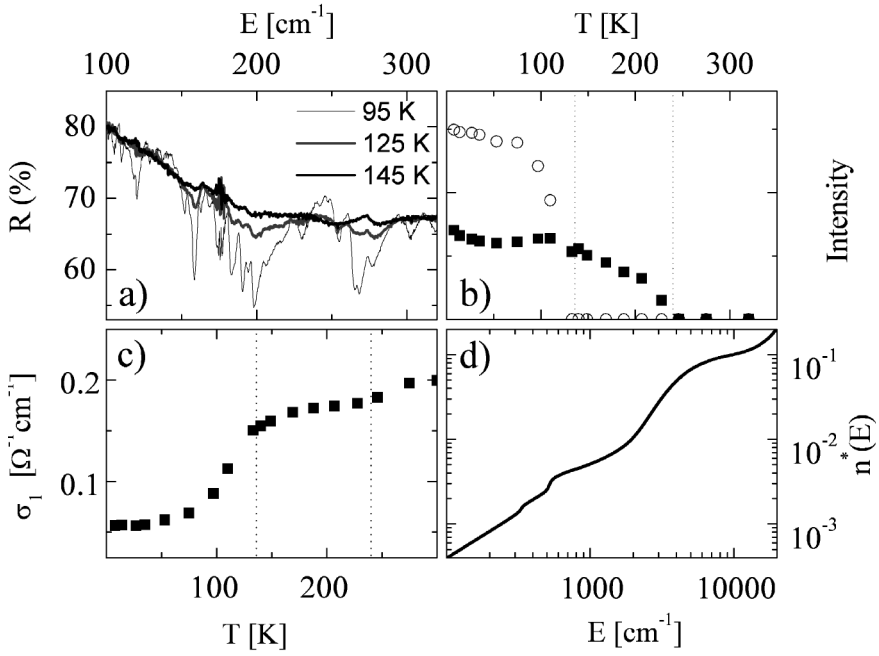


FIG. 3. (a) Detail of the reflectivity spectrum for $\mathbf{E} \parallel \mathbf{b}$ for $T = 95$, 125, and 145 K. (b) Temperature dependence of the intensity of two phonons appearing in the $\mathbf{E} \perp \mathbf{b}$ spectra at 990 $cm^{-1}$ (full symbols) and 950 $cm^{-1}$ (empty symbols). (c) Temperature dependence of the $\mathbf{E} \parallel \mathbf{b}$ optical conductivity for $E = 750$ $cm^{-1}$. (d) Effective number of electrons calculated from the $\mathbf{E} \parallel \mathbf{b}$ optical conductivity using Eq. (1).

An important clue for the interpretation of the optical spectra below 8000 $cm^{-1}$ is provided by the observation that, while a gap opens in the optical spectrum and the dc resistivity is below 136 K, the magnetic susceptibility is almost unaffected by the metal-insulator transition. If the gap were of the garden variety as in silicon, the spin fluctuations would become strongly suppressed below the same temperature where the optical conductivity becomes gapped. However, in $\beta$-$Na_{0.33}V_2O_5$ there is no formation of a spin gap when charge transport gets suppressed below 136 K [13]. This aspect of the data reflects the presence of strong on-site Hubbard-type repulsions between the charge carriers, which in one dimension causes the electrons to behave like spinless fermions, and it may thus be an experimental candidate for the material which can reproduce the main theoretical expectations of the partly occupied Hubbard chain: spin charge separation, and fractionalization of the charge [23]. The relative independence of the spin and charge channels has been noticed before for the Bechaard salts [24], the presence of a pseudogap in the optical excitations being opposed to the absence of a gap for spin excitations. Another important clue is provided by considering the optical response of the charge carriers: In a previous study [25], a minimum in the $E \parallel b$ reflectivity at 7200 $cm^{-1}$ has been attributed to a plasma edge. We can see from Fig. 2(a) that the main contribution to the oscillator strength associated with this plasma minimum arises from the prominent midinfrared band centered at 3000 $cm^{-1}$. By integrating the optical conductivity, and adopting the bare mass $m_e$ for the electrons, we calculated the effective number of electrons displayed in Fig. 3(d) using

$$8 \int_0^{\omega} \sigma_1(\omega') d\omega' = n^*(\omega) \frac{4\pi n_V e^2}{m_e}. \qquad (1)$$

The integrated spectral weight of the midinfrared feature corresponds to $n^*(10\,000\ cm^{-1}) \simeq 0.10$ electrons per V atom, which is rather close to the nominal chemical doping of $n = 0.166$ electrons per V atom. (The difference can be easily understood from the fact that in these transition metal oxides the effective mass of the electrons is about $2m_e$.) The high oscillator strength of the midinfrared peak as shown by the value of $n^*$ shows that it arises from the doped charge carriers. In contrast the spectral weight of the low frequency part up to 1500 $cm^{-1}$ is about 10% of the total midinfrared feature. Finally, the relative intensity of the low frequency spectral weight (in comparison to the 3000 $cm^{-1}$ peak) is almost independent of temperature above $T_{MI}$.

From studies of the Hubbard model in one dimension we know that part of the intraband spectral weight shows up as a band of midinfrared excitations. However, these studies have also demonstrated that, for doping far away from half filling of the Hubbard band, the intensity of the midinfrared band is less than 20% of Drude spectral weight [11,12]. This rules out an interpretation of the midinfrared peak in $\beta$-$Na_{0.33}V_2O_5$ in terms of a pure Hubbard model. At the same time we underscore the crucial role of Hubbard-type correlations for the independence of the spin response from the charge gap in this material.

The most trivial explanation of the 3000 $cm^{-1}$ peak would be that it is a direct transition between bands which are formed as a result of the umklapp potential of the Na superlattice below 240 K. However, the potential landscape caused by the Na ions becomes randomly ordered above 240 K. Although even a random potential would give rise to a midinfrared peak, the position of the midinfrared peak would become strongly temperature

dependent in such a scenario, in contrast to our experimental observations.

The remaining candidate for the midinfrared band is to assume that the charge carriers are small polarons. Derived basically from the Frank-Condon model, the small polaron peak [10] can be viewed classically as an instantaneous transition from a localized state to a neighboring localized state in a rigid ionic environment. The environment responds to the new electronic configuration by emitting a wave package of multiphonon oscillations, the envelope of which corresponds to the line shape of a polaron. It acquires not only a peak at several times the frequency of phonons but also a finite conductivity at low frequencies. The small polaron optical line shape, being influenced by the movement of ions, depends strongly on temperature [10]. This is indeed what we observe for the midinfrared feature in its high frequency part [see Fig. 2(a)].

The low frequency part is unchanged down to the $T_{MI} = 136$ K, in opposition to what is expected [10] and measured [26] for the small polarons. This unexpected behavior may have a connection to the disorder potential created by the Na atoms, which could smear out the influence of the temperature at low frequencies. If so, it would suggest that some disorder in the Na positions exists even below $T_{Na}$, in other words, that the ordering of the Na atoms takes place gradually. This is confirmed by the measured intensity of the 990 $cm^{-1}$ phonon which gradually develops in the insulating direction below $T_{Na}$, being fully developed at $T_{MI}$ [see Fig. 3(b)]. They both suggest that the MIT takes place at a temperature where the Na atoms are fully ordered. This strengthens the argument that the Na potential influences strongly the movement of the electrons on the V chains.

We summarize the interpretation of all optical features: Both the midinfrared peak at 3000 $cm^{-1}$ and the observation of strong electron-phonon coupling support the picture that the charge carriers in $\beta$-$Na_{0.33}V_2O_5$ should be regarded as small polarons. The strong Hubbard-type interactions are responsible for the observed independent behavior of the spin and charge channels at the metal-insulator phase transition. Below the phase transition the insulating state is a charge ordered phase. Future experiments will have to establish the detailed nature of the charge ordered state. Although in a way a regular array of polarons also represents a charge density wave (CDW), a distinguishing feature in this case is that in an ordinary CDW the spin and charge sectors should be gapped simultaneously, which clearly does not happen in $\beta$-$Na_{0.33}V_2O_5$ at 136 K, where the spin orders at a still lower temperature. The nature of the crystallographic phase transition at 136 K (i.e., the tripling of the unit cell along the chains) suggests that below 136 K the charges have become ordered with a commensuration of order 3 on the three different types of V chains and ladders in the unit cell. This would imply that the doped charges are either distributed equally over all V atoms or in a 2/3-1/3 ratio over the $V_1$ and $V_2$ atoms, resulting in a high degree of dilution. This a favorable condition for the formation of small polarons, consistent with the above interpretation of the spectra.

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