



## The symmetry problem in $\alpha'$ - $\text{NaV}_2\text{O}_5$

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### Abstract

We discuss the symmetry of  $\alpha'$ - $\text{NaV}_2\text{O}_5$  in the high temperature phase on the basis of optical conductivity data. Conclusive information cannot be obtained by studying the optically allowed lattice vibrations. However, intensity and polarization of the electronic excitations give a direct indication for a broken-parity electronic ground-state. This is responsible for the detection of *charged bi-magnons* in the optical spectrum. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:**  $\alpha'$ - $\text{NaV}_2\text{O}_5$ ;  $\text{CuGeO}_3$ ; Spin–Peierls transition; Charged magnons

The symmetry of  $\alpha'$ - $\text{NaV}_2\text{O}_5$  in the high temperature phase is the subject of intense discussion [1–3,9,10], because of its consequences on the interpretation of the phase transition at 34 K, ascribed to a spin-Peierls transition involving one-dimensional (1D) chains of  $\text{V}^{4+}$  ions [4]. This interpretation could be consistent with the non-centrosymmetric space group  $\text{P2}_1\text{mn}$  originally proposed by Carpy and Galy [1]. The structure of the compound consists of two-leg ladders running along the  $b$  axis, with the rungs oriented along the  $a$  axis and defined by two V ions, one on each leg of the ladder. In the space-group  $\text{P2}_1\text{mn}$ , the V d-electrons are distributed in such a way that the left and right legs of a ladder are formed by  $\text{V}^{4+}$  ( $S = 1/2$ ) and  $\text{V}^{5+}$  ( $S = 0$ ) ions, respectively. However, this structural analysis has recently been questioned and the centrosymmetric space group  $\text{Pmmn}$  has been proposed [2,9,10]: the V ions would have an average charge of +4.5 and it would not be possible to identify well distinct 1D magnetic chains. Therefore, the interpretation of the phase transition would not be straightforward.

A possible way to assess the symmetry issue is to investigate the Raman and infrared phonon spectra comparing

the number of experimentally observed modes with the number expected for the two space groups on the basis of a group-theoretical analysis. As a result of such a calculation we obtain for the irreducible representation of the optical vibrations for  $\text{P2}_1\text{mn}$ :

$$\Gamma = 15A_1(\text{aa,bb,cc};E||a) + 8A_2(\text{bc}) + 7B_1(\text{ab};E||b) + 15B_2(\text{ac};E||c),$$

corresponding to 45 Raman ( $A_1, A_2, B_1, B_2$ ) and 37 infrared ( $A_1, B_1, B_2$ ) active modes, and for  $\text{Pmmn}$ :

$$\Gamma' = 8A_g(\text{aa,bb,cc}) + 3B_{1g}(\text{ab}) + 8B_{2g}(\text{ac}) + 5B_{3g}(\text{bc}) + 7B_{1u}(E||c) + 4B_{2u}(E||b) + 7B_{3u}(E||a),$$

corresponding to 24 Raman ( $A_g, B_{1g}, B_{2g}, B_{3g}$ ) and 18 infrared ( $B_{1u}, B_{2u}, B_{3u}$ ) active modes. However, the number of observed phonons [3,5] is smaller than that calculated for both space groups, meaning that some of the optical vibrations in  $\alpha'$ - $\text{NaV}_2\text{O}_5$  have a very small oscillator strength. Therefore, an unknown number of modes has escaped detection in the experiments [3,5] and none of the two space groups can be ruled out.

A deeper understanding of the symmetry of  $\alpha'$ - $\text{NaV}_2\text{O}_5$  is obtained from the detailed analysis of the optical conductivity data [Fig. 1(b)], in particular when the electronic excitations are considered and compared to the result relative to  $\text{CuGeO}_3$  [Fig. 1(a)]. On the latter

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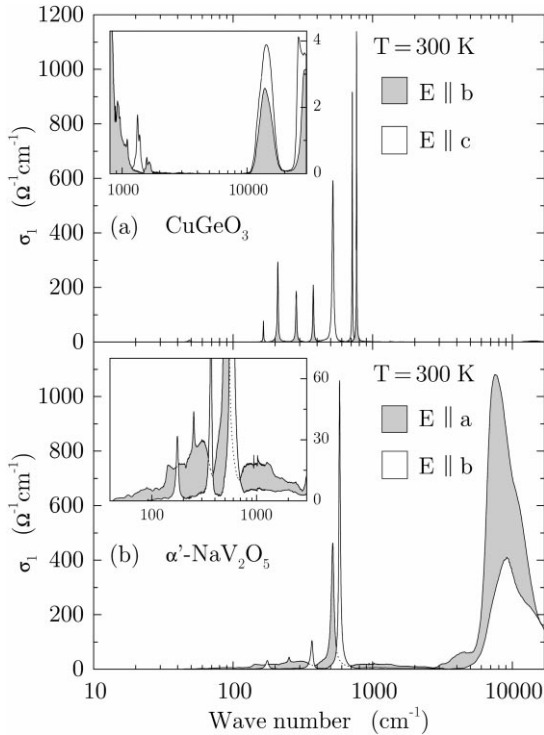


Fig. 1. Panel (a): optical conductivity of  $\text{CuGeO}_3$  at 300 K for  $E \parallel b$  (normal to the chains) and  $E \parallel c$  (along the chains). Inset: enlarged view of  $\sigma_1(\omega)$  from 800 to 30 000  $\text{cm}^{-1}$ . Panel (b): optical conductivity of  $\alpha'\text{-NaV}_2\text{O}_5$  at 300 K for  $E \parallel a$  (normal to the ladders) and  $E \parallel b$  (along the ladders). Inset: enlarged view of  $\sigma_1(\omega)$  from 40 to 3000  $\text{cm}^{-1}$ .

compound we observed sharp phonon lines below 1000  $\text{cm}^{-1}$  [6], multiphonon absorption at  $\sim 1500 \text{ cm}^{-1}$ , very weak [note the low values of  $\sigma_1(\omega)$  in the inset of Fig. 1(a)] phonon-assisted Cu d–d transitions at  $\sim 14000 \text{ cm}^{-1}$  [7], and the onset of the Cu–O charge-transfer (CT) excitations at  $\sim 26000 \text{ cm}^{-1}$ . On  $\alpha'\text{-NaV}_2\text{O}_5$ , besides the phonon lines in the far-infrared region, we detected features that are completely absent in  $\text{CuGeO}_3$ : a strong absorption peak at  $\sim 8000 \text{ cm}^{-1}$  and a low-frequency continuum for  $E \parallel a$  [inset of Fig. 1(b)]. On the basis of intensity considerations, the peak at  $\sim 8000 \text{ cm}^{-1}$  has to be ascribed to an optically allowed excitation and cannot be interpreted as a V d–d exciton, a transition that is in principle optically forbidden and only weakly allowed in the presence of a strong crystal field or electron–phonon coupling. The continuum along the  $a$  axis has to be due to double spin-flip excitations as the frequency range coincides with the low-energy scale spin excitations. Another reason for this assignment is the opening of a gap in the optical conductivity of  $17 \pm 3 \text{ meV}$  (i.e., approximately twice the spin gap value [8]), for  $T < 34 \text{ K}$  [3]. Moreover, intensity and polarization ( $E \parallel a$ ) of the continuum cannot be understood assuming the complete

equivalence of the V sites required by the space group Pmmn. In this case, in fact, direct and phonon-assisted spin excitations would be optically active along the ladders ( $E \parallel b$ ).

A way to understand qualitatively and quantitatively the electronic excitations in  $\alpha'\text{-NaV}_2\text{O}_5$  is to assume a broken left–right symmetry of the ladders, i.e., a difference  $\Delta$  between the on-site energies of the two V sites on the same rung. Each rung can be modeled as a polar diatomic molecule with, e.g., left bonding ( $L_B$ ) and right anti-bonding ( $R_{AB}$ ) lob-sided wave functions. An electron can then be optically excited from the  $L_B$  to the  $R_{AB}$  orbital and it is this on-rung CT between the two V sites that we identify with the strong absorption peak at  $\sim 8000 \text{ cm}^{-1}$ . From the frequency and the integrated intensity of the CT absorption we can calculate  $\Delta \approx 0.8 \text{ eV}$  and the on-rung hopping parameter  $|t_{\perp}| \approx 0.3 \text{ eV}$ , and show that the valence of the two V ions on a rung is 4.1 and 4.9, respectively [3]. We now consider a small segment of the ladder consisting of three rungs, and one electron per rung in the  $L_B$  orbital. If the spins are anti-parallel, the middle electron undergoes some virtual hopping to the two neighboring rungs and, for  $U \rightarrow \infty$ , it will eventually reside in a  $R_{AB}$  orbital. If the spins are parallel (i.e., if the middle spin has been flipped over), no virtual hopping is possible because of the Pauli principle. As a result, there is a net dipole displacement perpendicular to the legs between the two different configurations: spin-flip excitations carry a finite dipole moment which is responsible for the detection of *charged bi-magnons* in the optical spectrum for  $E \parallel a$ , i.e., a *direct two-magnon optical absorption*. It can be shown that the effective charge for this process is  $q_m = q_e(3J_{\parallel}\Delta/\Delta^2 + 4t_{\perp}^2)$ , where  $q_e$  is the electron charge and  $J_{\parallel}$  is the exchange coupling constant between two spins on neighboring rungs [3]. Therefore, for a symmetrical ladder, where  $\Delta = 0$ ,  $q_m = 0$  and the charged magnon effect disappears. On the other hand, for an asymmetrically charged ladder  $q_m \neq 0$ . It is clear from the argument above that the symmetry has to be broken only locally to obtain optical activity of two-magnon excitations: it is sufficient to have short chain segments of at least three spins, which are randomly distributed between left and right legs of the ladders.

In conclusion, by analyzing the optical conductivity, we showed that intensity and polarization of the electronic excitations give a direct evidence for a broken-parity electronic ground-state of  $\alpha'\text{-NaV}_2\text{O}_5$  in the high temperature phase. The broken symmetry is responsible for the detection of charged bi-magnons in the optical spectrum.

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