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Published in:
Physical Review Letters

Publication date:
1998

The symmetry problem in α'-NaV_2O_5

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(29 May 1998)

We discuss the symmetry of α'-NaV_2O_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.

Keywords: α'-NaV_2O_5; $CuGeO_3$; spin-Peierls transition; charged magnons

The symmetry of α'-NaV_2O_5 in the high temperature phase is the subject of intense discussion [1–3] 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 V^{4+} [4]. This interpretation could be consistent with the non-centrosymmetric space group $P2_1mn$ 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 $P2_1mn$, the V d-electrons are distributed in such a way that the left and right legs of a ladder are formed by V^{4+} (S=1/2) and V^{5+} (S=0) ions, respectively. However, this structural analysis has recently been questioned and the centrosymmetric space group $Pmmn$ has been proposed [2]: 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 (R) and infrared (IR) phonon spectra comparing the number of experimentally observed modes with the number expected for the two space groups on the basis of a group-theory analysis. As a result of such a calculation we obtain for the irreducible representation of the optical vibrations for $P2_1mn$:

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

corresponding to 45 R (A_1,A_2,B_1,B_2) and 37 IR (A_1,B_1,B_2) active modes, and for $Pmmn$:

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

corresponding to 24 R (A_g,B_{1g},B_{2g},B_{3g}) and 18 IR (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 α'-NaV_2O_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.

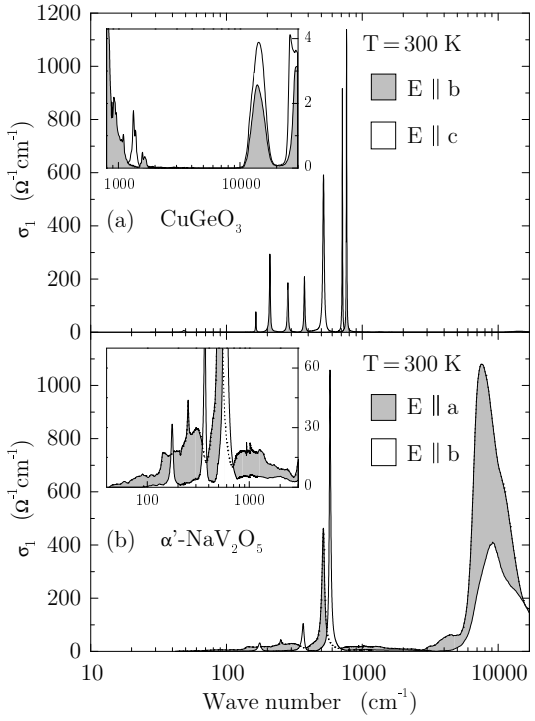

FIG. 1. Panel (a): optical conductivity of $CuGeO_3$ at 300 K for $\vec{E} \| \vec{b}$ (normal to the chains) and $\vec{E} \| \vec{c}$ (along the chains). Inset: enlarged view of $\sigma_1(\omega)$ from 800 to 30 000 cm^{-1}. Panel (b): optical conductivity of α'-NaV_2O_5 at 300 K for $\vec{E} \| \vec{a}$ (normal to the ladders) and $\vec{E} \| \vec{b}$ (along the ladders). Inset: enlarged view of $\sigma_1(\omega)$ from 40 to 3000 cm^{-1}.

A deeper insight of the symmetry of α'-NaV_2O_5 is obtained from optical conductivity data [Fig. 1(b)], in particular when compared to the result relative to $CuGeO_3$ [Fig. 1(a)]. On the latter compound we observed sharp phonon lines below 1000 cm^{-1} [6], multiphonon absorptions at ∼1500 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 ∼14 000 cm^{-1} [7], and the onset of the Cu-

O charge-transfer (CT) excitations at $\sim$26 000 cm^{-1}. On α'-NaV_2O_5, besides the phonon lines in the far-infrared region, we detected features that are completely absent in $CuGeO_3$: a strong absorption peak at $\sim$8000 cm^{-1} and a low-frequency continuum for $\vec{E} \parallel \vec{a}$ [inset of Fig. 1(b)]. On the basis of intensity considerations, the peak at $\sim$8000 cm^{-1} has to be ascribed to an optically allowed excitation and cannot be interpreted as a V *d-d* exciton, a transition that is in principle optically forbidden and only weakly allowed in the presence of a strong crystal field or electron-phonon coupling. The continuum along the *a* axis, as the frequency range coincides with the low-energy scale spin excitations, has to be due to double spin-flip excitations. Another reason for this assignment is the opening, for T<34 K [3], of a gap in the optical conductivity of 17±3 meV (*i.e.*, approximately twice the spin gap value [8]). Moreover, intensity and polarization ($\vec{E} \parallel \vec{a}$) of the continuum cannot be understood assuming the complete equivalence of the V sites required by the space group *Pmmn*. In fact, direct and phonon-assisted spin excitations, if characterized by a finite intensity, would be optically active along the ladders ($\vec{E} \parallel \vec{b}$).

A way to understand qualitatively and quantitatively the electronic excitations in α'-NaV_2O_5 is to assume a broken left-right symmetry of the ladders, *i.e.*, a difference Δ 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 cm^{-1}. From the integrated intensity of the CT absorption we can calculate $\Delta \approx 0.8$ eV and the on-rung hopping parameter $|t_\perp| \approx 0.3$ 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 with three rungs, and one electron per rung in the L_B orbital. If the spins are anti-parallel, the middle electron experiences some virtual hopping to the two neighboring rungs and, for $U \to \infty$, 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 $\vec{E} \parallel \vec{a}$, *i.e.*, a *direct two-magnon optical absorption*. It can be shown that the effective charge for this process is $q_m = q_e \frac{3J_\parallel \Delta}{\Delta^2 + 4t_\perp^2}$, 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 Δ=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 α'-NaV_2O_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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