Infrared study of spin-Peierls compound \( \alpha'\)-NaV\(_2\)O\(_5\)^* 

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Abstract

Infrared reflectance of \( \alpha'\)-NaV\(_2\)O\(_5\) single crystals in the frequency range from 50 cm\(^{-1}\) to 10000 cm\(^{-1}\) was studied for \( a \), \( b \) and \( c \)-polarisations. In addition to phonon modes identification, for the \( a \)-polarised spectrum a broad continuum absorption in the range of 1D magnetic excitation energies was found. The strong near-IR absorption band at 0.8 eV shows a strong anisotropy with vanishing intensity in \( c \)-polarisation. Activation of new phonons due to the lattice dimerisation were detected below 35K as well as pretransitional structural fluctuations up to 65K.

Keywords: \( \alpha'\)-NaV\(_2\)O\(_5\) ; spin-Peierls transition ; phonons.

Recently, a spin-Peierls (SP) transition was found in inorganic compounds CuGeO\(_3\) and \( \alpha'\)-NaV\(_2\)O\(_5\) \([1, 2]\). The evidence of structural phase transition in \( \alpha'\)-NaV\(_2\)O\(_5\) was obtained, first, by observation of additional superlattice X-ray reflections \([3]\), and then by measurements of new phonon lines in infrared (IR) \([4, 5]\) and Raman \([6]\) spectra below \( T_{SP} \approx 35\) K. The 1D magnetic properties of \( \alpha'\)-NaV\(_2\)O\(_5\) were explained on the basis of the non-centrosymmetric space group \( P2_11mn \) as initially determined \([7]\).

Room temperature IR reflectance was measured in the frequency range between 50 cm\(^{-1}\) and 10000 cm\(^{-1}\) on two \( \alpha'\)-NaV\(_2\)O\(_5\) single crystals grown according to the procedure described in Ref. \([8]\). For transmission measurements \( \alpha'\)-NaV\(_2\)O\(_5\) powder was ground in KBr and pressed in pellets. The IR measurements were done with a Bruker IFS 113V Fourier spectrometer with a resolution ranging from 1 cm\(^{-1}\) in the far-IR region to 5 cm\(^{-1}\) in the near-IR region. The low temperature spectra were measured with a continuous He flow cryostat with the absolute accuracy of temperature control about 0.1 K. Reference spectra (reflectance of the freshly evaporated gold film or direct transmittance) were measured after each sample spectrum measurement.

The 300K polarised reflectivity \( R(\nu) \) spectra of \( \alpha'\)-NaV\(_2\)O\(_5\) are shown in Fig.1. From the factor group analysis one should expect 37 IR active phonon modes for the non-centrosymmetric structure: \( \Gamma(P_{21mn})_{IR} = 15A_1(E \parallel a) + 7B_1(E \parallel b) + 15B_2(E \parallel c) \), or 18 modes for the recently proposed \([9]\) centrosymmetric one: \( \Gamma(P_{mmn})_{IR} = 7B_{1u}(E \parallel c) + 4B_{2u}(E \parallel b) + 7B_{3u}(E \parallel a) \). We observed 6 \( a \)-polarised, 4 \( b \)-polarised and 5 \( c \)-polarised phonons. This information does not allow to choose between two space groups since some phonons may have too small oscillator strengths to be detected.

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In order to quantitatively describe $R(\nu)$ spectra, we applied the classical approach based on a harmonic oscillator model assuming that all transitions (either electronic or phonon) provide a Lorenzian contribution to the dielectric function:

$$\varepsilon(\nu) = \varepsilon_\infty + \sum_j \nu_j^2 \frac{\nu_{S,j}^2}{\nu_j^2 - \nu^2 - i\gamma_j \cdot \nu}$$

where $\varepsilon_\infty$ is the high frequency dielectric constant; $\nu_j$, $\nu_{S,j}$, $\gamma_j$ are the frequency, the oscillator strength and the damping of the $j$-th oscillator (for the phonons $\nu_j=\nu_{TO}$). Calculated reflectivity spectrum is fitted to the experimental one starting from the $\nu_j$, $\nu_{S,j}$, $\gamma_j$ values determined using Kramers-Kronig analysis. In the region of phonon frequencies ($\nu < 1000 \text{ cm}^{-1}$), the $R(\nu)$ spectra have a typical form of phonon bands in an insulating material only for b- and c- polarisation. In order to describe the $R(\nu)$ spectrum for a-polarisation, it is necessary to introduce in the dielectric function two wide Lorenzian "continuum" bands centred at approximately 280 cm$^{-1}$ and 1100 cm$^{-1}$. Let us note that these energies ($\approx 400$ K and 1580K, respectively) fall in the energy range of magnetic excitations in a Heisenberg S=1/2 spin chain (the nearest-neighbour intrachain constant in $\alpha'$-NaV$_2$O$_5$ is $J \approx 440 \div 560$ K [1,2]). This "continuum" might result from a direct two-magnon absorption mechanism recently suggested in Ref. [10]. It could also involve a phonon assisted two-magnon scattering process [11]. On the other hand, the near-IR strong optical transition found for $E\parallel a$ was explained recently as a charge transfer (CT) absorption mechanism between two on-rung V sites [10]. Following this approach, one can calculate the energy difference between V sites on the same rung (a-direction) $\Delta \approx 0.6$ eV and the hopping constant $t_{\perp} \approx 0.33$ eV. Then, the estimated valence state of the vanadium atoms is 4.2 and 4.8.

All phonon modes with $\nu_{TO}>200 \text{ cm}^{-1}$ except the weak $E\parallel c$ mode at 583 cm$^{-1}$ were also observed in transmission spectra of $\alpha'$-NaV$_2$O$_5$ powder dispersed in KBr pellets. Below $T_{SP}$ we detected 6 new lines at 363, 411, 716, 969, 1275, 1399 cm$^{-1}$. The pellets technique is especially useful to analyse phonon modes with different oscillator strength. We use this method to complete the study of the evolution with temperature of the strongest new phonon line at $\approx 718 \text{ cm}^{-1}$ [5]. Detailed temperature dependence of the above line shown in Fig. 2 gives a clear evidence of precursor effects up to at least 64K. The observation of pretransitional spectral signatures at $T>T_{SP}$ linked to the new phonon in the SP state indicates the existence of local structural fluctuations likely driven by 1D magnetic fluctuations via strong magnetoelastic coupling.

In conclusion, first IR measurements of $\alpha'$-NaV$_2$O$_5$ along all three $a$, $b$ and $c$-polarisations are reported. An anomalous behaviour along $a$-polarisation is evidenced by both a low frequency continuum involving spin excitations and near-IR charge transfer band. Pretransitional structural fluctuations are observed in a wide temperature range above $T_{SP}$.

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References

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Table 1. Oscillator parameters (in cm\(^{-1}\)) used to fit the IR reflectivity spectra of \(\alpha\)'-NaV\(_2\)O\(_5\).

|       | \(E\parallel a (\varepsilon_\infty = 2.6)\) |       |       |       |       |
|-------|--------------------------------|-------|-------|-------|-------|
| \(\nu_{TO}\) | 940 | 522 | 252 | 146.7 | (*)  |
| \(\nu_{S,TO}\) | 42  | 853 | 87  | 62   |       |
| \(\gamma_{TO}\) | 8.2 | 28.4| 9.6 | 8.8  |       |

“Continuum” contribution: 1). \(\nu = 278\), \(\nu_S = 472\), \(\gamma = 209\); 2). \(\nu = 1109\), \(\nu_S = 647\), \(\gamma = 522\). CT contribution: 1). \(\nu = 3970\), \(\nu_S = 4120\), \(\gamma = 2260\); 2). \(\nu = 6540\), \(\nu_S = 11970\), \(\gamma = 2550\)

|       | \(E\parallel b (\varepsilon_\infty = 1.5)\) |       |       |       |       |
|-------|--------------------------------|-------|-------|-------|-------|
| \(\nu_{TO}\) | 580  | 366 | 230 | 176  |       |
| \(\nu_{S,TO}\) | 1046 | 291 | 32  | 107  |       |
| \(\gamma_{TO}\) | 14.9 | 12.1| 10.1| 6.8  |       |

CT contribution: \(\nu = 7280\), \(\nu_S = 12780\), \(\gamma = 7160\)

|       | \(E\parallel c (\varepsilon_\infty = 3.0)\) |       |       |       |       |
|-------|--------------------------------|-------|-------|-------|-------|
| \(\nu_{TO}\) | 954  | 583 | 468 | 182  | 164  |
| \(\nu_{S,TO}\) | 589  | 90  | 219 | 207  | 55.6 |
| \(\gamma_{TO}\) | 3.7  | 58  | 36.9| 10.5 | 3.2  |

* - lines at 740 cm\(^{-1}\) and 90 cm\(^{-1}\) are observed at T<100K

Figure captions.

Fig. 1. 300K polarised reflectivity spectra of \(\alpha\)'-NaV\(_2\)O\(_5\) single crystal. The solid lines represent the calculated spectra. Not all the experimental points are shown for the sake of clarity.

Fig. 2. Temperature dependence of the (716-718) cm\(^{-1}\) line. Open circles and squares indicate the integral intensity of the transmittance (716 cm\(^{-1}\)) and reflectivity (718 cm\(^{-1}\)) line, respectively. The solid triangles show the intensity of Lorenzian component deduced from reflectivity data as described in Ref. 3.
Wave number (cm$^{-1}$)

$R$ (%)
