

# Pressure-dependent infrared properties of the quasi-one-dimensional metal $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$

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In quasi-one-dimensional metals electron–phonon coupling in general plays an important role, often leading to a Peierls instability with the opening of an energy gap at the Fermi level. The electron–phonon coupling can also cause local lattice distortions surrounding the charge carriers, resulting in a self-trapping of the charges, thus forming polarons. A characteristic signature of polarons in the optical response is a pronounced absorption band in the mid-infrared (MIR) range. Recently, such a band was also observed in the quasi-one-dimensional metal  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$  for the polarization along the conducting axis, and it was interpreted in terms of small-polaron excitation [1].  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$  undergoes three temperature-induced phase transitions at ambient pressure [2], including a metal–insulator transition around 135 K caused by the charge ordering on the V sites. In direct vicinity to the charge-ordered phase, superconductivity was found for tempera-

tures below 10 K and pressures  $P$  above 7 GPa [3]. At  $P \approx 9$  GPa superconductivity is suppressed again. Up to now the nature of the superconducting phase, in particular the relation to the charge order and the role of polaronic quasiparticles, is unclear.

We studied the polarization-dependent MIR reflectivity of  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$  at room temperature as a function of pressure  $P$ . Details about the experiment and analysis of the data can be found in Ref. [4]. In Fig. 1 the optical conductivity for the low ( $P < 12$  GPa) and high ( $P > 12$  GPa) pressure regime and for the polarization along and perpendicular to the conducting direction  $b$  is presented. Up to 12 GPa the oscillator strength of the pronounced  $\mathbf{E} \parallel b$  MIR band increases with increasing pressure and its maximum shifts to lower frequencies [see Fig. 1(a)]. For  $\mathbf{E} \perp b$  the optical conductivity monotonically increases; this increase is most pronounced in the low-frequency ( $\omega < 3000 \text{ cm}^{-1}$ ) range. The three sharp phonon modes near  $1000 \text{ cm}^{-1}$  in the  $\mathbf{E} \perp b$ -spectra [see inset of Fig. 1(c)] harden in a sublinear fashion [4]. For pressures above 12 GPa the observed trends in the optical behavior

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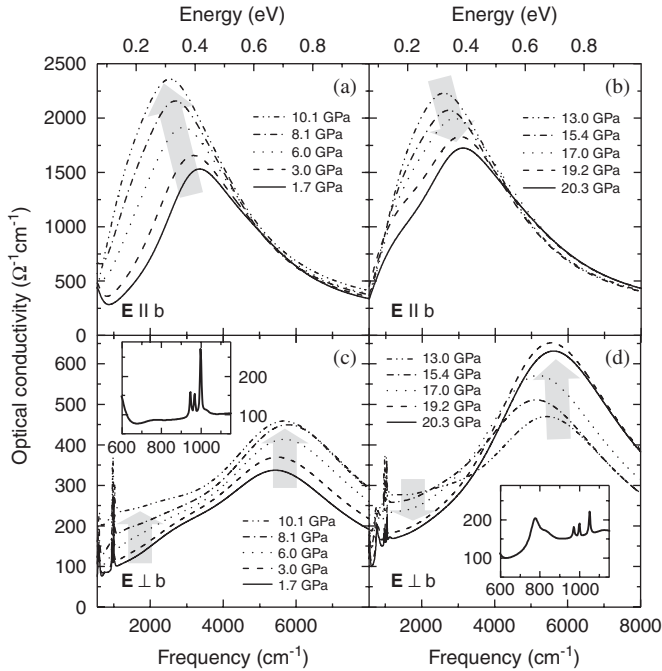


Fig. 1. Pressure-dependent optical conductivity spectra of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  at room temperature for the polarization  $\mathbf{E}$  parallel [(a) and (b)] and perpendicular [(c) and (d)] to the chain direction  $b$ . The arrows illustrate the changes with increasing pressure. Insets: enlargements of the low-frequency  $\mathbf{E} \perp b$  optical conductivity for the lowest and highest applied pressure.

change markedly [Fig. 1(b) and (d)]: the MIR absorption band observed for  $\mathbf{E} \parallel b$  shifts to higher frequencies and its oscillator strength decreases, in contrast to the low-pressure regime. For  $\mathbf{E} \perp b$  the low-frequency ( $\omega < 3000 \text{ cm}^{-1}$ ) part of the optical conductivity spectrum also decreases, whereas in the high-frequency ( $\omega > 3000 \text{ cm}^{-1}$ ) part the conductivity continues to increase. The hardening of the three sharp  $\mathbf{E} \perp b$  phonon modes prevails in the high-pressure regime. Furthermore, in the  $\mathbf{E} \perp b$  spectra new, relatively broad excitations evolve [see inset of Fig. 1(d)], consisting of a pronounced mode around  $750 \text{ cm}^{-1}$  with a shoulder on its high-frequency side. Similar to the phonon modes near  $1000 \text{ cm}^{-1}$ , these features show a hardening with increasing pressure. An explanation of the new excitations in terms of an amorphization of the sample can be excluded, since the basic structural motif remains intact up to the highest applied pressure, as evidenced by the smooth pressure dependence and sharpness of the three optical phonons for  $\mathbf{E} \perp b$ . Also the reversibility of the observed pressure-induced spectral changes make a pressure-induced amorphization at 12 GPa unlikely to have occurred in our experiment. A structural phase transition appears unlikely as well, since the observed features develop continuously with increasing pressure for  $P > 12 \text{ GPa}$ , and traces of them are seen already at lower pressures. The new modes might be the result of a pressure-induced ordering of the Na

atoms, leading to a zone-folding due to superstructure formation. Another interesting aspect is a possible pressure-induced redistribution of charge between crystallographically inequivalent vanadium sites, leading to the appearance of additional phonon modes. An interplay between structural changes, like polyhedral distortion, and charge redistribution for  $P > 12 \text{ GPa}$  is also possible, since the pressure dependence of the  $\mathbf{E} \parallel b$  MIR band completely changes at  $P = 12 \text{ GPa}$ .

The pressure dependence of the MIR band for  $\mathbf{E} \parallel b$  is of particular interest, since it was claimed to be of small-polaronic origin [1]. Within small-polaron theory the frequency of the polaron band is a measure of the polaron binding energy [5], and thus of an electron-phonon coupling. In general, the electron-phonon coupling tends to decrease under pressure as a result of the combined band broadening and stiffening of the crystal lattice. So, one expects a decrease of the polaron binding energy under pressure to be a common trend. Therefore, the observed redshift of the MIR band with increasing pressure appears to be consistent with its claimed polaronic origin. If the polaronic quasiparticles were to survive up to  $P = 12 \text{ GPa}$ , their possible role for the superconductivity in  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  could not be ruled out.

An important point is the reduction of the strong anisotropy of the electronic properties under pressure. The increase in the low-frequency optical conductivity for  $\mathbf{E} \perp b$  below 12 GPa indeed indicates a pressure-induced dimensional crossover from 1D to 2D (or 3D), with an enhanced interchain coupling. The trend is, however, reversed at around the pressure where superconductivity is suppressed. This observation raises the question, whether a certain magnitude of interchain electronic coupling is required to stabilize the superconducting state in  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ . This scenario may serve as a starting point to understand why superconductivity is limited to a rather narrow range of pressures. To clarify this point, pressure-dependent optical measurements at low temperature are highly desirable.

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