Joint 20th AIRAPT – 43th EHPRG, June 27 – July 1, Karlsruhe/Germany 2005

Infrared properties of the quasi-one-dimensional superconductor β-$Na_{0.33}V_2O_5$ under pressure

C.A. Kuntscher, 1. Physikalisches Institut, Universität Stuttgart, Stuttgart, Germany, kuntscher@pi1.physik.uni-stuttgart.de*

S. Frank, 1. Physikalisches Institut, Universität Stuttgart, Stuttgart, Germany

I. Loa and K. Syassen, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany

T. Yamauchi and Y. Ueda, Institute of Solid State Physics, University of Tokyo, Tokyo, Japan

Summary

Pressure-dependent optical properties in the mid-infrared range are presented for the quasi-one-dimensional superconductor β-$Na_{0.33}V_2O_5$ at room temperature. The observed changes of the spectra for pressures up to 12 GPa suggest a pressure-induced dimensional crossover and the relevance of electron-phonon coupling. Above 12 GPa, the spectra exhibit pronounced changes, in particular the development of new excitations, possibly due to a redistribution of charge and/or subtle structural changes. A possible relation between the interchain coupling and superconductivity is pointed out.

Introduction

Superconductivity was recently observed in the low-dimensional β-$Na_{0.33}V_2O_5$ at high pressures of 7–9 GPa and in proximity to a charge-ordered phase (Yamauchi, 2002). This compound is the first vanadium oxide exhibiting superconductivity, and it is the first observation of a transition from a charge-ordered to a superconducting state in a pressure-temperature phase diagram. The one-dimensional metallic character of β-$Na_{0.33}V_2O_5$ (Wallis, 1977; Yamada, 1999) can be related to its crystal structure consisting of three kinds of chains based on three crystallographically inequivalent V sites (see Fig. 1): zigzag double chains composed of edge-sharing (V1)O_6 octahedra, two-leg ladders composed of corner-sharing (V2)O_6 octahedra, and zig-zag double chains of edge-sharing (V3)O_5 polyhedra. All chains are oriented along the *b* axis (Wadsley, 1955). At ambient pressure, β-$Na_{0.33}V_2O_5$ undergoes three phase transitions as a function of temperature (Yamada, 1999; Ueda, 2001): (i) ordering of the sodium ions at 240 K, (ii) a metal-insulator transition around 135 K caused by charge ordering on the V sites (Heinrich, 2004) due to electronic correlations, and (iii) an antiferromagnetic transition at 22 K.

Besides the importance of electronic correlations causing the charge ordering, electron-phonon coupling appears to be relevant for the electronic conduction mechanism. A pronounced absorption band centered at 3000 cm^{-1} was found in the optical conductivity spectra for the polarization **E** parallel to the conducting axis *b* and interpreted in terms of the photoionization of small polarons (Presura, 2003). The influence of polaronic effects on the electronic structure is supported by angle-resolved photoemission spectroscopy (Okazaki, 2004). However, up to now the importance of electron-phonon coupling and charge ordering for the pressure-induced superconductivity in β-$Na_{0.33}V_2O_5$ is unclear. We carried out high-pressure, polarization-dependent mid-infrared reflectivity experiments on β-$Na_{0.33}V_2O_5$ at room temperature. The experiments serve as a first step towards the understanding of the nature of the superconducting phase and its relation to the charge ordering and interchain coupling. In this paper we also address the issues of electron-phonon coupling and pressure-induced structural changes.

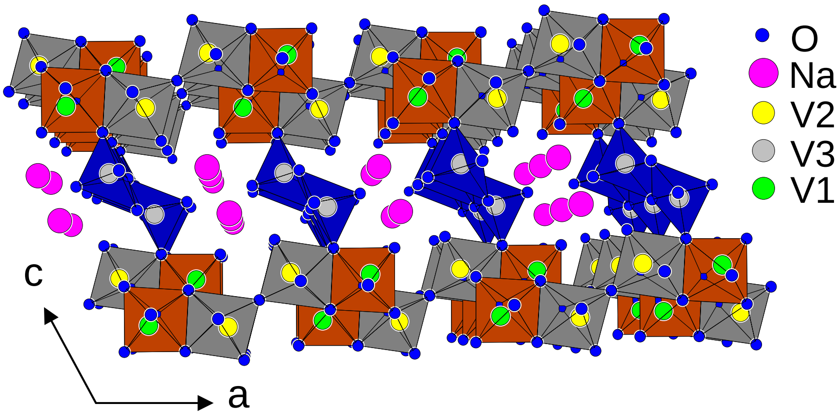

Fig. 1. Monoclinic crystal structure of β-$Na_{0.33}V_2O_5$ ($a = 10.08$ Å, $b = 3.61$ Å, $c = 15.44$ Å, $\beta = 109.6°$), consisting of three kinds of chains built by three crystallographically inequivalent V sites: zigzag double chains composed of edge-sharing $(V1)O_6$ octahedra, two-leg ladders composed of corner-sharing $(V2)O_6$ octahedra, and zig-zag double chains of edge-sharing $(V3)O_5$ polyhedra, oriented along the *b* axis (Wadsley, 1955).

Experimental Method

The infrared reflectivity measurements were carried out on single crystals showing a sharp metal-insulator transition around 135 K. A diamond anvil cell equipped with type IIA diamonds suitable for infrared measurements was used for the generation of pressures up to 20 GPa. Finely ground KCl powder was chosen as a quasi-hydrostatic pressure-transmitting medium. Two single crystals were polished to a thickness of about 40 μm. For each pressure experiment, a small piece (about 80 μm x 100 μm in size) was cut from one of the thin platelets and placed in the hole (150 μm diameter) of a steel gasket. A ruby chip was added for determining the pressure by the ruby luminescence method (Mao, 1986). Polarization-dependent reflectivity measurements in the mid-infrared frequency range (550-8000 cm^{-1}) at room temperature were carried out partly with a laboratory setup at the University of Stuttgart using a conventional radiation source and partly at the infrared beamline of the synchrotron radiation source ANKA (Karlsruhe). The reproducibility of the results was checked by performing six experimental runs on different pieces of the two crystals. A Bruker IFS 66v/S FT-IR spectrometer was employed for the measurements. To focus the beam onto the small sample in the pressure cell, an infrared microscope (Bruker IRscope II) coupled to the spectrometer and equipped with a 15x magnification objective was used. Reflection spectra were measured at the interface between the sample and the diamond anvil. Spectra taken at the inner diamond-air interface of the empty cell served as a reference for normalization of the sample spectra. All reflectivity spectra reported here refer to the absolute reflectance at the sample-diamond interface, which is denoted as $R_{s\text{-}d}$. Optical conductivity spectra were obtained by fitting the reflectivity data with the Drude-Lorentz model combined with the normal-incidence Fresnel equation, taking into account the known refractive index of diamond. More details about the normalization and fitting of the reflectance spectra are published elsewhere (Kuntscher, 2005).

Results

Pressure-dependent reflectivity spectra are presented in Fig. 2 for the optical polarizations $\mathbf{E}||b$ and $\mathbf{E}\perp b$ (i.e., $\mathbf{E}||c$) and for pressures below and above 12 GPa. The corresponding optical conductivity spectra are shown in Fig. 3. Up to $P = 12$ GPa, the overall reflectivity rises monotonically with increasing pressure for both polarizations, indicating a growing spectral weight in the infrared response. Correspondingly, the oscillator strength of the pronounced **E** || *b* mid-infrared band in the optical conductivity increases [Fig. 3(a)], and its maximum shifts to lower frequencies. The most notable effect on the **E**⊥*b*-spectra is a steep increase of $R_{s\text{-}d}$ in the low-frequency ($\omega < 2000$ cm^{-1}) range [Fig. 2(c)]. The increase in spectral weight is directly seen in the low-frequency optical conductivity, shown in Fig. 3(c).

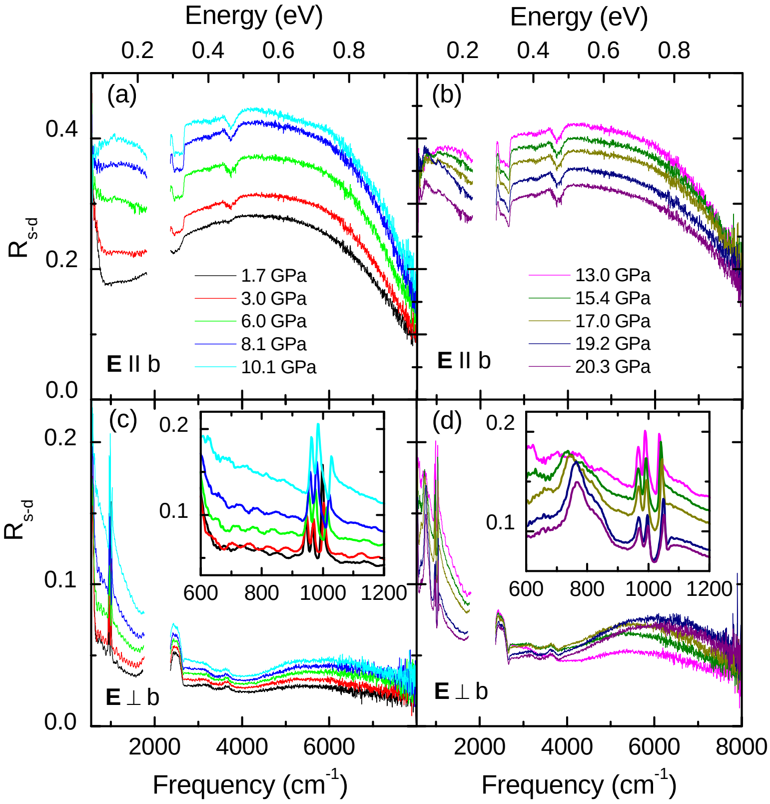

Fig. 2: Room-temperature reflectivity spectra of β-$Na_{0.33}V_2O_5$ as a function of pressure for the polarization **E** parallel to the *b*-axis [(a) and (b)] and perpendicular to the *b*-axis [(c) and (d)]. Insets: Enlargements of the low-frequency reflectivity for **E**⊥*b*.

The observed trends in the optical behavior change markedly at around $P = 12$ GPa (see Figs. 2 and 3). An overall *decrease* of the reflectivity with increasing pressure is observed for **E** || *b*. In the corresponding optical conductivity spectra [Fig. 3(b)], the mid-infrared band shifts to higher frequencies and its oscillator strength decreases – in contrast to the low-pressure regime. In the perpendicular direction, the low-frequency ($\omega < 3000$ cm^{-1}) part of the reflectivity spectrum also decreases, whereas the high-frequency ($\omega > 3000$ cm^{-1}) reflectivity continues to increase. Furthermore, new and relatively broad excitations appear in the **E**⊥*b* spectra [see insets of Figs. 2(d) and 3(d)]. They consist of a pronounced peak at around 750 cm^{-1} and a shoulder on the high-frequency side. In pressure-dependent Raman data of the related compounds CaV_2O_5 and $NaVO_3$, broad modes with comparable frequencies were found for pressures above 6 GPa and 9 GPa, respectively (Popovic, 2002; Shen, 1994). These features were attributed to a pressure-induced amorphization of the samples. This is clearly in contrast to β-$Na_{0.33}V_2O_5$, where the basic structural motif remains intact up to the highest applied pressure, as is evidenced by the smooth pressure dependence and sharpness of the three optical phonons for **E**⊥*b*. A pressure-induced amorphization of β-$Na_{0.33}V_2O_5$ at 12 GPa can therefore be excluded. This is also supported by the reversibility of the observed pressure-induced spectral changes.

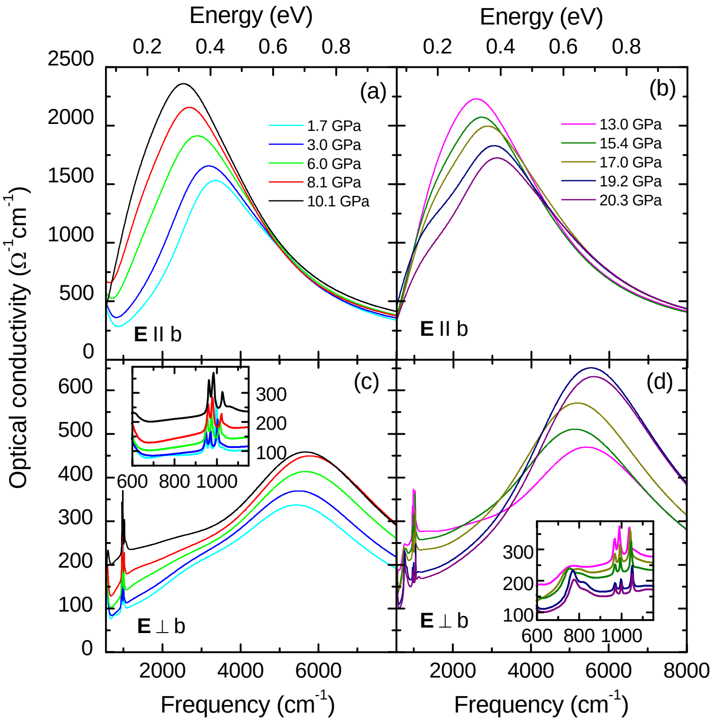

Fig. 3: Pressure-dependent optical conductivity spectra of β-$Na_{0.33}V_2O_5$ at room temperature for the polarization **E** parallel to the chain direction *b* [(a) and (b)] and perpendicular to *b* [(c) and (d)], obtained by Drude-Lorentz fits to the reflectivity data. Insets: Enlargements of the low-frequency optical conductivity for **E**⊥*b*.

Discussion

The pressure dependence of the mid-infrared absorption band for **E** || *b* is of particular interest, since it was claimed to be of small-polaronic origin (Presura, 2003). Within small-polaron theory, the frequency of the polaron band is a measure of the polaron binding energy (Emin, 1993) and thus of the electron-phonon coupling. In general, the electron-phonon coupling tends to decrease under pressure as a result of the combined electronic band broadening and stiffening of the crystal lattice. A decrease of the polaron binding energy under pressure is thus expected to be a common trend. The observed redshift of the mid-infrared band with increasing pressure appears therefore to be consistent with its claimed polaronic origin. If the polaronic quasiparticles were to survive up to $P = 12$ GPa, their possible role for the superconductivity in β-$Na_{0.33}V_2O_5$ could not be ruled out. On the other hand, pressure-induced structural rearrangements (like polyhedral tilts and distortions) could also affect the electron-phonon coupling. And whether the optical response could be explained in terms of interband-like excitations not involving polarons is considered to be still an open question.

The appearance of new low-energy excitations for **E**⊥*b* alerts us of the possibility that the reversal of trends in the oscillator strength at around 12 GPa could be linked to a structural phase transition. However, the additional spectral features develop continuously with increasing pressure for $P > 12$ GPa, and traces of them are seen already at lower pressures. A structural phase transition thus appears unlikely. 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 scenario is a pressure-induced redistribution of charge between the crystallographically inequivalent vanadium sites. As was suggested recently (Heinrich, 2004), the charges are primarily located on the V1 sites, with a minor occupation of the V2 sites. One could speculate that upon pressure application a partial transfer of charge from the V1 to the V2 sites occurs, resulting in an enhanced coupling of the incident electromagnetic field to some phonon modes. An interplay between structural changes, like polyhedral distortion, and charge redistribution for $P > 12$ GPa is also possible, since the pressure dependence of the **E** || *b* mid-infrared band changes completely at $P = 12$ GPa.

An important point is the reduction of the strong anisotropy of the electronic properties under pressure. The steep increase in the low-frequency reflectivity for **E**⊥*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 β-$Na_{0.33}V_2O_5$. This scenario may serve as a starting point to understand why superconductivity is limited to a rather narrow range of pressures.

Conclusions

In conclusion, we have studied the pressure-dependent mid-infrared reflectivity of β-$Na_{0.33}V_2O_5$ at room temperature for two different polarization directions **E** of the incident radiation. The redshift of the mid-infrared absorption band for **E** || *b* and pressures up to 12 GPa is compatible with a polaronic picture. However, an interpretation in terms of interband-like excitations cannot be ruled out. The appearance of new low-energy excitations for **E**⊥*b* might be due to a pressure-induced ordering of the Na atoms or a redistribution of charges between crystallographically inequivalent vanadium sites. A pressure-induced dimensional crossover is found in the low-pressure ($P < 12$ GPa) regime. The reversal of this trend above 12 GPa raises the question whether a certain magnitude of interchain electronic coupling is required to stabilize the superconducting state in β-$Na_{0.33}V_2O_5$.

Acknowledgements

The provision of beamtime by the Angströmquelle Karlsruhe (ANKA) is gratefully acknowledged, and we thank D. Moss, Y.-L. Mathis, and B. Gasharova for support at the ANKA infrared beamline. Financial support by the DFG (Emmy Noether-program) is acknowledged.

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