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

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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. From the monotonic changes of the spectra for pressures below 12 GPa a pressure-induced dimensional crossover and the relevance of electron-phonon coupling can be inferred. The major changes in the spectra above 12 GPa, in particular the development of new excitations, may be due to a redistribution of charge with a possible relation to structural changes. Furthermore, a possible relation between the interchain coupling and the superconducting order is printed out.

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The interrelation of charge order phenomena and superconductivity recently raised interest in several low-dimensional systems. A prominent example is the ordering of charges in the form of stripes in the high-temperature copper oxide superconductors,[1] whose influence on the superconductivity is still under debate.[2] Also the closely related quasi-one-dimensional (quasi-1D) spin chain and ladder compounds $Sr_{14-x}Ca_xCu_{24}O_{41}$ show a rich phase diagram including a charge-ordered and a superconducting phase.[3] Further examples are the two-dimensional organic BEDT-TTF salts, where the proximity of the charge ordering to the superconducting state in the phase diagram of some compounds[4] led to a possible explanation of the superconducting pairing mediated by charge fluctuations.[5]

A similar phase diagram was recently found for the low-dimensional vanadate β-$Na_{0.33}V_2O_5$.[6] The anisotropy of its metallic character[7,8] can be explained by its crystal structure 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.[9] At ambient pressure β-$Na_{0.33}V_2O_5$ undergoes three phase transitions:[8,10] ordering of the sodium ions at 240 K, a metal-insulator transition around 135 K caused by charge ordering on the V sites[11] due to electronic correlations, and an antiferromagnetic transition at 22 K. Recently, the pressure-temperature phase diagram was investigated by dc resistivity and ac susceptibility measurements for pressures *P* up to 9 GPa.[6] A superconducting phase in proximity to the charge-ordered phase was found for temperatures below 10 K and pressures higher than 7 GPa. At $P \approx 9$ GPa superconductivity is suppressed again.

Besides the importance of electronic correlations, the relevance of electron-phonon interactions for the conduction mechanism of β-$Na_{0.33}V_2O_5$ was suggested already quite early.[12] Furthermore, the recent observation of an absorption band centered at 3000 cm^{-1} in the optical conductivity spectra for the polarization **E** parallel to the conducting axis *b* was interpreted in terms of polaronic excitations.[13] The influence of polaronic effects on the electronic structure was supported by angle-resolved photoemission.[14] However, up to now the importance of electron-phonon coupling and charge ordering for the superconductivity in β-$Na_{0.33}V_2O_5$ is unclear.

In this paper we present a polarization-dependent mid-infrared reflectivity study on β-$Na_{0.33}V_2O_5$ at room temperature as a function of pressure. According to the pressure dependences of the electronic and vibrational features, two pressure regimes exist. In the low pressure regime ($P \leqslant 12$ GPa) the overall reflectivity increases monotonically with increasing pressure along both studied directions, indicating an increasing conductivity of the compound. At $P \approx 12$ GPa significant changes occur, including the appearance of new modes. 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. We also address the issues of electron-lattice coupling and pressure-induced structural changes.

Single crystals were grown according to Ref. 8. The quality of the crystals used for the high-pressure experiments was checked by dc resistivity measurements showing a sharp metal-insulator transition around 135 K. The reflectivity spectra of the free-standing polished samples were found to be in good agreement with earlier results.[13] 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 quasi-hydrostatic pressure medium. Two single crystals were polished to a thickness of ≈ 40 μm. For each pressure experiment a small piece (about 80 μm $\times$ 100 μm in size) was cut from one thin platelet and placed in the hole of a steel gasket. A ruby chip was added for determining the pressure by the ruby luminescence method.[15]

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. The reproducibility of the results was ensured by six experimental runs on different pieces of two crystals. A Bruker IFS 66v/S FT-IR spectrometer was

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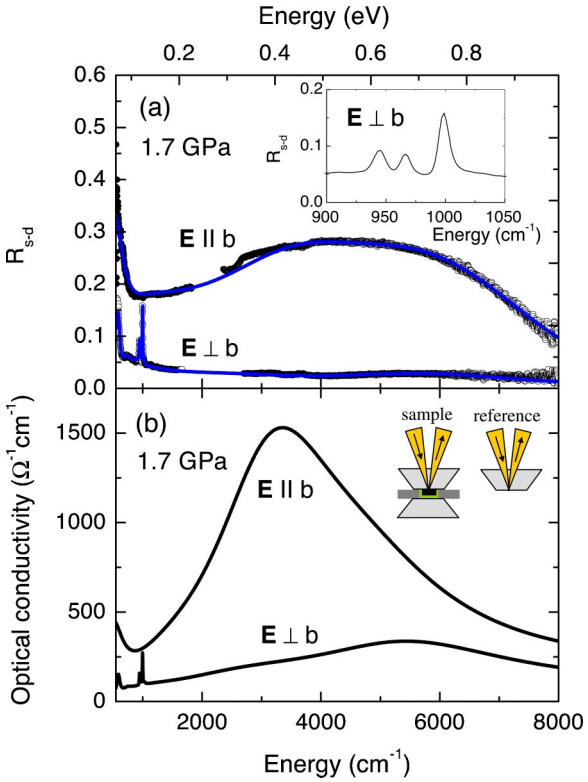

FIG. 1. (Color online) (a) Room-temperature reflectivity spectra R_{s-d} of β-$Na_{0.33}V_2O_5$ inside the diamond anvil cell at $P=1.7$ GPa for the polarization **E** parallel and perpendicular to the chain direction b. The blue lines are fits of the reflectivity spectra with the Drude-Lorentz model. Inset: Enlargement of the low-frequency range of the $\mathbf{E}\perp b$ reflectivity spectrum showing three sharp optical phonon modes. (b) Optical conductivity spectra obtained from the Drude-Lorentz fits of the reflectivity data. Inset: Geometries for the sample and reference measurements.

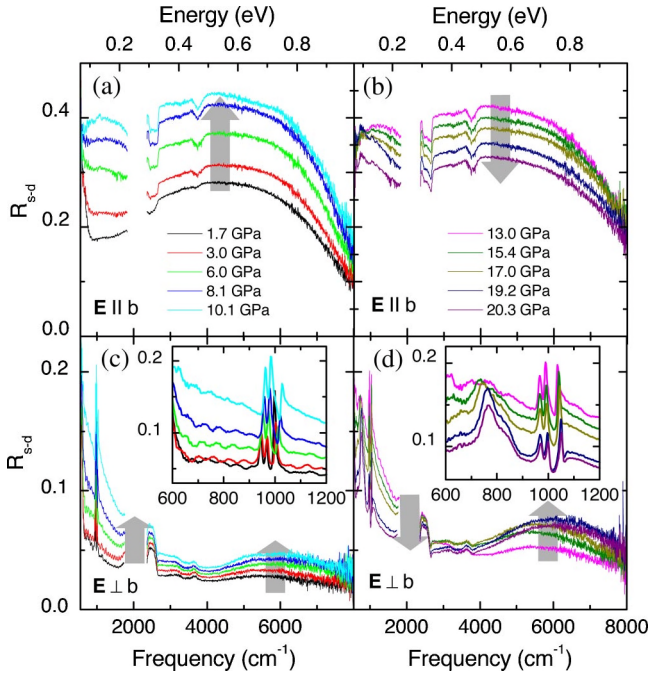

FIG. 2. (Color online) Room-temperature reflectivity spectra of β-$Na_{0.33}V_2O_5$ as a function of pressure for the polarization **E** parallel and perpendicular to the b axis. Insets: Enlargements of the low-frequency reflectivity for $\mathbf{E}\perp b$.

employed for the measurements. To focus the beam on the small sample in the pressure cell, an infrared microscope (Bruker IRscope II) coupled to the spectrometer and equipped with a 15× magnification objective was used. Reflection spectra were measured at the interface between sample and diamond anvil [see inset of Fig. 1(b)]. Spectra taken at the inner diamond-air interface of the empty cell served as the reference for normalization of the sample spectra. Variations in source intensity were taken into account by applying additional normalization procedures. All reflectivity spectra reported below refer to the absolute reflectivity at the sample-diamond interface which is denoted as R_{s-d}.

Polarization-dependent reflectivity and optical conductivity spectra for the lowest investigated pressure ($P=1.7$ GPa) are shown in Fig. 1. The region around 2000 cm^{-1} is cut out from the experimental spectra because the diamond multi-phonon absorption causes artifacts in this range. The overall reflectivity of the sample in the diamond anvil cell as compared to that of the free-standing sample[13] is lower due to the smaller refractive index step at the sample-diamond interface. To obtain the corresponding optical conductivity, the reflectivity spectra were fitted with the Drude-Lorentz model combined with the normal-incidence Fresnel equation, taking into account the known refractive index of diamond. For the lowest applied pressure an overall agreement with previous ambient-pressure results[13] was obtained. For the polarization **E** along the chain direction b we observe a relatively strong mid-infrared band centered at 3000 cm^{-1}, which had been assigned to polaronic excitations.[13] For $\mathbf{E}\perp b$ (i.e., $\mathbf{E}\|c$) the optical conductivity spectrum consists of a group of three prominent optical phonons at around 1000 cm^{-1} and a broad band centered around 5500 cm^{-1}.

Pressure-dependent reflectivity spectra are presented in Fig. 2 for the polarizations $\mathbf{E}\|b$ and $\mathbf{E}\perp b$ and for pressures below and above 12 GPa. The features at $\omega\approx 2500$ and 3700 cm^{-1} might be due to multiphonon absorptions of diamond which appear due to uniaxial stresses in the diamond anvils at high pressure. Corresponding optical conductivity spectra for $\mathbf{E}\|b$ are shown in Fig. 3. In the Drude-Lorentz fits an increase of the background dielectric constant (by 15% at maximum) according to the Clausius-Mossotti relation[16] was assumed to account for the pressure-induced reduction of the unit cell volume.[17] Up to $P=12$ GPa the overall reflectivity along both directions rises monotonically with increasing pressure, indicating a growing spectral weight in the infrared response. Correspondingly, the oscillator strength of the pronounced $\mathbf{E}\|b$ mid-infrared band in the optical conductivity increases [Fig. 3(a)]; its maximum shifts to lower frequencies. The most notable effect on the $\mathbf{E}\perp b$ spectra is a steep increase of R_{s-d} in the low-frequency ($\omega<3000$ cm^{-1}) range. In Fig. 4(a) we plot the peak positions of the three sharp phonon features seen near 1000 cm^{-1} in the $\mathbf{E}\perp b$ spectra as a function of applied pressure [for spectra see insets of Figs. 2(c) and 2(d)]. The modes harden in a sublinear fashion, with the initial linear pressure coefficients ranging from 1.9 to 3.3 cm^{-1}/GPa.

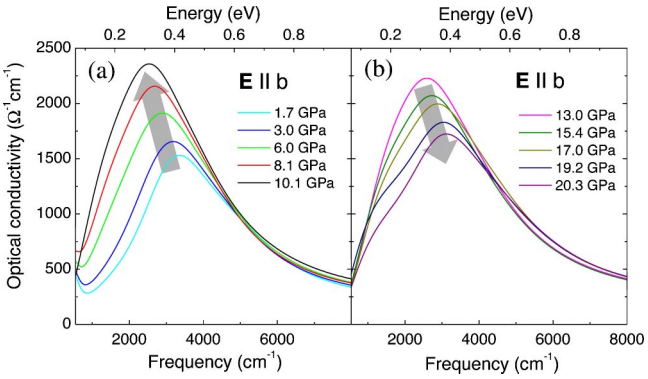

FIG. 3. (Color online) Pressure-dependent optical conductivity spectra of β-$Na_{0.33}V_2O_5$ at room temperature for the polarization **E** parallel to the chains, obtained by Drude-Lorentz fits of the reflectivity data.

The observed trends in the optical behavior change markedly for pressures above $P=12$ GPa (Fig. 2). An overall *decrease* of the reflectivity with increasing pressure is observed for $\mathbf{E}\|b$. 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 in the high-frequency ($\omega>3000$ cm^{-1}) part the reflectivity continues to increase. The hardening of the three sharp $\mathbf{E}\perp b$ phonon modes prevails in the high pressure regime [Fig. 4(a)]. The smoothness of the frequency shifts with pressure indicates that at least the local V-O coordination does not undergo any major changes at pressures up to 20 GPa. Furthermore, in the $\mathbf{E}\perp b$ spectra new, relatively broad excitations evolve [see inset of Fig. 2(d)], consisting of a pronounced mode around

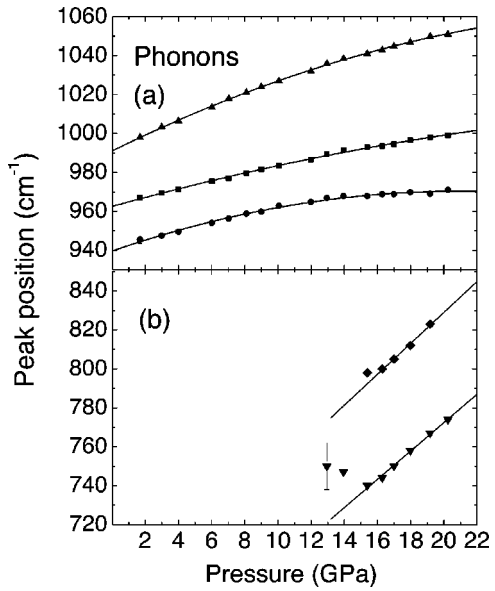

FIG. 4. Peak positions of (a) the three optical phonons for $\mathbf{E}\perp b$ as a function of pressure, and (b) the new excitations evolving for $\mathbf{E}\perp b$ at $P>12$ GPa. The lines are polynomial fits of the data.

750 cm^{-1} with a shoulder on its high-frequency side. Similar to the phonon modes near 1000 cm^{-1}, these features show a hardening with increasing pressure [see Fig. 4(b)], however, at a larger rate (7.2 and 7.9 cm^{-1}/GPa, respectively). For the related compounds CaV_2O_5 and $NaVO_3$ broad modes with comparable frequencies were found for pressures above 6 and 9 GPa, respectively,[18,19] and attributed to an 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 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.

The optical spectra described above contain valuable information about the electronic and structural properties of the quasi-1D compound β-$Na_{0.33}V_2O_5$ under pressure. We will first concentrate our discussion of results on the low-pressure regime ($P<12$ Gpa). One finding is the absence of discontinuous changes in the electronic and vibrational features at $P=7$ GPa, where superconductivity is induced.[6] Actually, no hints for structural changes are found for pressures below 12 GPa, in agreement with x-ray diffraction measurements under pressure.[17]

The pressure dependence of the mid-infrared band for $\mathbf{E}\|b$ is of particular interest, since it was claimed to be of small-polaronic origin.[13] Within small-polaron theory the frequency of the polaron band is a measure of the polaron binding energy,[20] 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 mid-infrared band with increasing pressure appears 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 still to be an open question.

The appearance of new low-energy excitations for $\mathbf{E}\perp b$ alerts us of the possibility that the reversing of trends in the oscillator strength at around 12 GPa could be linked to a structural phase transition. However, the observed 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 aspect is a pressure-induced redistribution of charge between crystallographically inequivalent vanadium sites. As was suggested recently,[11] 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 $\mathbf{E} \| b$ mid-infrared band completely changes 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 $\mathbf{E} \perp b$ 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 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.

The proximity of superconductivity to the charge-ordered state in the phase diagram of β-$Na_{0.33}V_2O_5$ led to the idea that superconductivity is mediated by charge fluctuations.[6] A pressure-induced redistribution of charge as discussed above would be a new facet to this scenario. In addition, the influence of polaronic effects on the electronic properties cannot be neglected, as evidenced by optical and photoemission results.[13,14] With our pressure-dependent optical data we add another important piece of information to the puzzling picture of the superconductivity in β-$Na_{0.33}V_2O_5$: the possible relevance of polaronic quasiparticles for the superconductivity; they may survive up to at least $P = 12$ GPa as indicated by the effect of pressure on the mid-infrared absorption band. Furthermore, we propose a relation between the interchain coupling and the superconducting order. For a full understanding of the possible influence of charge ordering, polaronic effects, and dimensionality on the superconductivity in β-$Na_{0.33}V_2O_5$ and other low-dimensional materials, pressure-dependent optical investigations at low temperature appear highly promising.

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