RESONANT RAMAN SCATTERING IN NaV_2O_5 AS A PROBE OF ITS ELECTRONIC STRUCTURE

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Abstract

In order to investigate the origin of the phase transition observed in NaV_2O_5, as well as its electronic structure, we have measured Raman intensities as a function of the laser wavelength above and below the phase transition temperature. In the polarized Raman spectra at room temperature we observe resonant enhancement of the 969 cm^{-1} phonon mode when the laser energy approaches 2.7 eV, presumably related to the (p-d) electron hopping band, $O_3(p_y)$-$V(d_{xy})$, at 3.2 eV. The 969 cm^{-1} mode originates from the stretching vibrations along the c-axis involving the V-O_1 bonds. Since an ellipsometric determination of the dielectric function ϵ_{cc} yields no structure in the 1.7 to 5.5 eV photon energy range, we conclude that plane bonds couple strongly with the apical oxygens leading to a large Raman efficiency. In the low-temperature Raman spectra, almost all modes that become active below the phase transition temperature T_c=34 K show resonant behavior. The most interesting ones, those at 66 and 106 cm^{-1}, possibly of magnetic origin, exhibit a resonant intensity enhancement, approximately by an order of magnitude, for laser photon energies around 1.85 eV with respect to 2.43 eV. This resonance effect may be associated with a weak absorption band around 2 eV. Finally, a destructive interference between the resonant and the nonresonant contribution to the Raman scattering amplitude (i.e. an antiresonance) is found in the spectra for most of the (bb) low-temperature modes.

I. INTRODUCTION

NaV_2O_5 has been reported to be the second inorganic spin-Peierls compound [1], following $CuGeO_3$, with a phase transition temperature T_c=34 K. However, recent experimental findings suggest a different character for the phase transition of NaV_2O_5 as compared to that of $CuGeO_3$ [2]. NaV_2O_5 is believed to be a nearly perfect realization of a quarter-filled low-dimensional system, with possible charge ordering below the critical temperature. Such a scenario is supported by structural analysis [3], nuclear magnetic resonance experiments

[4] and Raman scattering studies [5]. These results indicate that the V ions are equivalent at room temperature and in a mixed-valent state, $V^{4.5+}$. When lowering the temperature below T_c the V sites change their valence from uniform to alternating V^{4+} and V^{5+} [4]. Two different models for the electronic ordering in the low-temperature phase have been discussed. One is described as in-line [6] with the V^{4+} ions arranged along the legs of the ladder (**b**-axis) and the other one with the V^{4+} ions arranged in a zig-zag manner along the **b**-axis [7,8]. The first one requires an additional phase transition, like the ordinary spin-Peierls transition, for an opening of the spin-gap. For the second one it is argued that a spin-gap appears due to the zig-zag ordering itself [8]. However, in both cases the driving mechanism for a particular charge ordering has not been elucidated. In the Raman spectra this transition manifests itself through the appearance of new modes whose origin is still not fully understood [9–11]. In general, Raman scattering intensities are strongly correlated with the electronic structure of solids. Their determination as a function of the laser photon energy yields information about the energies of interband transitions and their orbital character as has been highlighted recently by resonance Raman measurements on high- temperature superconductors [12]. Having this in mind, we have measured Raman intensities as a function of the laser wavelength, both above and below the phase transition temperature. On the basis of the observed effects we discuss the origin of the resonances and the electronic structure of NaV_2O_5.

II. EXPERIMENT

The measurements were performed on single crystals, with a size of approximately 1x3x1 mm^3 along the **a**, **b**, and **c** axis, respectively, prepared as described in [1]. As exciting source we used eight lines from Ar^+ and Kr^+ ion lasers, with photon energies between 1.55 to 2.71 eV. The laser beam, with an average power of 5 mW, was focused on the (001) surface of the crystals. The spectra were measured in back-scattering geometry using a Dilor XY triple monochromator equipped with a CCD camera. Comparable relative Raman intensities were obtained by normalizing the measured spectra with respect to the calibrated spectral emission density of an Ulbricht sphere system (Opto-Electronik Reiche GmbH), thus taking care of the varying spectral response of both spectrometer and detector over the large wavelength range investigated.

III. HIGH TEMPERATURE SPECTRA

The room temperature Raman spectra in $c(aa)\bar{c}$ and $c(bb)\bar{c}$ polarized configurations are presented in Fig. 1a) and b). In the (aa) spectra seven phonon modes are clearly seen with an additional broad continuum peaked at 650 cm^{-1}. In this geometry all modes, as well as the continum, decrease in intensity with decreasing laser photon energy. In the spectra measured with energies lower than 2 eV the appearance of an additional continuum centered at about 170 cm^{-1} is observed. In contrast to the (aa) spectra, most peaks in the (bb) spectra do not vary much with the laser line used, except for the 534 cm^{-1} mode. According to a lattice dynamical calculation [13], the 969 cm^{-1} mode originates from apical oxygen vibrations (V-O_1 stretching vibrations) along the **c**-axis. The increase of its (aa)

intensity with increasing laser energy can be related to the resonance of the incoming (or scattered) laser light with the strong electronic absorption band at 3.22 eV, observed by ellipsometry [14]. According to LMTO calculations [15] this band represents the excitation of electrons hopping from the $O_3(p_y)$ to the V(d_{xy}) orbital. Since the dielectric function along the c-axis has no structure in the 1.7 to 5.5 eV range, we conclude that plane bonds strongly couple with the apical oxygen leading to a large Stokes-Raman efficiency, $S_{xx}(O_1)$. Similarly, an electronic band related to $O_3(p_x)$-V(d_{xy}) hopping is found along the **b**-axis at 3.73 eV [14]. We thus expect a large intensity for the (bb) 969 cm^{-1} phonon at a laser energy around 3.7 eV. One can use similar arguments for the resonant behavior of other phonons with displacements that influence the O-V hopping. The (aa) modes with energies of 448 and 534 cm^{-1} overlap with the broad continuum centered at 650 cm^{-1} and exhibit typical Fano-type lineshapes [16]. We analyse the lineshape of the 535 cm^{-1} mode by fitting to the standard Fano expresion [16]. The fitting parametar q^{-1} is plotted vs. excitation energy in the inset of Fig.1. From the linear extrapolation we obtain a resonance energy of E_0=0.9 0.2 eV. This energy can be associated with a large absorption band centered around 1-1.2 eV [17,18], observed in both the **E**||**a** and the **E**||**b** optical absorption spectra. This band has been tentatively assigned to d-d transitions [17,18]. In the literature there is still no consensus as to whether the 1 eV band can be assigned to a d-d transition energy within the t-J model using a reasonable range of parameters, with [18,19] or without [20] charge disproportionation. An even more controversial issue concerns the existence of low energy excitations in these models, as a possible explanation for broad features found in IR and Raman spectra [12,13].

IV. LOW TEMPERATURE SPECTRA

The low-temperature (T=10 K) (aa) and (bb) Raman spectra are given in Fig. 2a) and b). We find new modes that become active below the phase transition temperature, T_c=34 K, due to the doubling of the unit cell. This doubling can be explained by assuming the charge-ordering scenario with a zig-zag ordering pattern of the charges [21]. Almost all new modes show resonant behavior. The lowest frequency modes with energies at 66 and 106 cm^{-1}, previously assigned to magnetic excitations [10], exhibit an increase in intensity by approximately an order of magnitude when using a laser photon energy around 1.85 eV (with respect to that at 2.43 eV) in (aa) polarized spectra. The intensity of the the 66 cm^{-1} mode is plotted in Fig. 3b) (aa - polarization) and Fig. 4b) (bb - polarization) as a function of the laser energy. In the same figures we show ϵ_2^a and ϵ_2^b for comparison, taken from [14], respectively. The peak at 1.85 eV of the 66 cm^{-1} mode intensity in (aa) polarization occurs close to the broad structure centered around 2 eV . The electronic transitions around 2 eV consist of two bands centered at 2 and 2.1 eV. Their low absorption strength, energy position and band separation of about 0.1 eV are typical for crystal- field transitions of d-elements. Thus, it is possible that these two absorption bands correspond to crystal-field-excitations of V^{4+} ions from the ground xy state to $x^2 - y^2$ and to $3z^2 - r^2$ states. The intensity behavior of the 66 cm^{-1} mode in (bb) polarization is quite different: Intensity is increasing with increasing laser energy and has a local minimum around 2.2 eV. Again, such behavior is not easy to understand from simple comparisom with ϵ_2 and more correct analyses are necessary to clarify these effects. The difference in the resonance behavior of the 948 cm^{-1} mode in

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the (aa) and the (bb) spectra, shown in Fig. 3c) and Fig. 4c), is also of interest. While in the case of the (aa) spectrum this mode looses intensity with decreasing laser energy, its behavior in the (bb) spectra is exactly the opposite. The origin of this effect is not clear. However, it has been argued by Riera and Poilblanc [22] that a zig-zag pattern of charges in a ladder can be stabilized by the Holstein coupling and the nearest-neighbor Coulomb repulsion. This indicates the importance of electron-phonon interaction as a possible driving mechanism for charge-ordering in NaV_2O_5. If the 948 cm^{-1} phonon is somehow involved in charge ordering (via electron-phonon coupling) it would see such a particular electronic structure [22] in its resonanace behaviour. Finally, we discuss the possible antiresonant behavior around 2.2 eV, suggested by comparison of Fig. 4a) and d). Such an effect usually results from an cancellation of resonant and nonresonant contributions to the scattering amplitude. Correspondingly, the cross section becomes very small below (or above) the critical point energy. However, it is also possible that there are two resonances, one at 1.7 eV and one around 2.5 eV. Thus phonons are resonant either only at 1.7 eV (Fig. 3b, 4c), only at 2.5 eV (Fig. 3c), or at both energies (Fig. 4b, d). To resolve these possibilities more acurate measurements are required.

V. CONCLUSION

In conclusion, we have presented measurements of Raman intensities as a function of the laser wavelength above and below the phase transition temperature. We have found that various phonons show significant resonances around 1.8 and 2.5 eV. The first one can be probably associated with weak crystal-field absorption bands around 2 eV, while the second one may corresponds to the band which represents the excitations of electrons hopping from the $O_3(p_y)$ to the $V(d_{xy})$ orbitals.

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FIGURES

FIG. 1. Room temperature Raman spectra of NaV_2O_5 single crystals measured with several laser energies in a) $c(aa)\bar{c}$ and b) $c(bb)\bar{c}$ scattering configurations. L denotes plasma lines. Inset: a plot of q^{-1} versus excitation energy as obtained by fitting the line shape of the 534 cm^{-1} phonon.

FIG. 2. Raman spectra of NaV_2O_5 single crystals at T=10 K measured with several laser energies in a) $c(aa)\bar{c}$ and b) $c(bb)\bar{c}$ scattering configurations. L denotes plasma lines.

FIG. 3. a) ϵ_2^a at T=25 K, taken from [14]. Intensity of b) 66 cm^{-1} mode and c) 948 cm^{-1} mode as a function of laser energy (T=10 K).

FIG. 4. a) ϵ_2^b at T=25 K, taken from [14]. Intensity of b) 66 cm-1, c) 948 cm-1 mode, d) 398 cm-1 mode as a function of laser energy (T=10 K).

Inset axis labels and annotations:

534 cm^{-1} phonon

$E_0 = 0.9 \pm 0.2$ eV

q^{-1} (vertical axis, 0.0 to 0.5)

Energy (eV) (horizontal axis, 0.8 to 2.8)

a)

(aa)

T=300 K

752.5 nm

676.4 nm

568.2 nm

514.5 nm

457.9 nm

L

L

Intensity (arb. units)

Raman shift (cm^{-1})

(aa) T=10 K a)

752.5 nm

676.4 nm

647.1 nm

568.2 nm

488.0 nm

Intensity (arb. units)

Raman shift (cm^{-1})