A new X-ray diffraction study of the one-dimensional spin-Peierls compound $\alpha’$-Na$_2$V$_2$O$_5$ reveals a centrosymmetric (Pmmn) crystal structure with one type of V site, contrary to the previously postulated non-centrosymmetric $P2_1mn$ structure with two types of V sites ($V^{+4}$ and $V^{+5}$). Density functional calculations indicate that Na$_2$V$_2$O$_5$ is a quarter-filled ladder compound with the spins carried by V-O-V molecular orbitals on the rungs of the ladder. Estimates of the charge-transfer gap and the exchange coupling agree well with experiment and explain the insulating behavior of Na$_2$V$_2$O$_5$ and its magnetic properties.

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**Introduction** Two classes of quasi one-dimensional compounds with spin-gaps have been investigated intensively in the last few years, ladder systems like SrCu$_2$O$_3$ and Sr$_{1.4}$Cu$_{2.4}$O$_{4.1}$ and spin-Peierls compounds like CuGeO$_3$ and $\alpha’$-Na$_2$V$_2$O$_5$. For even-leg ladder systems the spin-gap is structurally induced and present at all temperatures (for an overview see [10]). The possibility of superconductivity in doped ladder systems has been discussed [3] and found in Sr$_2$Ca$_{1.2}$Cu$_{2.4}$O$_{4.1}$ under pressure [2]. A spin-Peierls system undergoes a lattice instability at $T_{SP}$ and for $T<T_{SP}$ the system dimerizes and a spin-gap opens. Here we propose that the spin-Peierls compound Na$_2$V$_2$O$_5$ is at the same time a quarter-filled ladder system, in contrast to the previous notion which assumed Na$_2$V$_2$O$_5$ to be made up of weakly coupled pairs of $V^{+4}$ and $V^{+5}$ chains [2,3]. Our proposition is based on a re-determination of the crystal structure of Na$_2$V$_2$O$_5$ by X-ray diffraction and on density-functional calculations. Mapping of the density functional results on Hubbard and Heisenberg models yields values for the model parameters which explain readily the insulating behavior of Na$_2$V$_2$O$_5$ and its the magnetic properties. Our results also show that Na$_2$V$_2$O$_5$ and Ca$_2$V$_2$O$_5$ are isostructural and consequently establish Ca$_2$V$_2$O$_5$ as a half-filled ladder system.

**Crystal structure** The crystal structure of $\alpha’$-Na$_2$V$_2$O$_5$ consists of double chains of edge-sharing distorted tetragonal VO$_5$-pyramids running along the orthorhombic b-axis, which are linked together via common corners of the pyramids to form sheets. These in turn are stacked upon each other along c with no direct V-O-V links (see Fig. 1a and 1b). The Na atoms are located between these sheets. In their original papers Galy et al. and Carpy et al. [1] proposed the non-centrosymmetric space group $C_{2v}^{+}P2_1mn$ for this mixed valence compound (on average $V^{+4.5}$). After the discovery of a spin-Peierls transition in $\alpha’$-Na$_2$V$_2$O$_5$ at $T_{SP}=34$ K [4], it has been argued that the charge ordering would lead to a magnetic decoupling of adjacent double chains [1,3] and would be responsible for the one-dimensional character of this compound observed in magnetic susceptibility measurements [4,8].

![FIG. 1. a) Crystal structure of Na$_2$V$_2$O$_5$. The diamonds denote the position of the oxygen O(1)- and O(2)-ions which form the basal quadrangles of the VO$_3$ pyramids oriented in $\pm z$ directions. Also shown are the apex O(3) and the Na positions. The dashed line indicates the intersection of the plane for the charge density plot of Fig. 2. b) Hopping matrix elements of our effective V($d_{xy}$) Hamiltonian.](image-url)
essentially unchanged with respect to previous results. The possibility for long range charge ordering, however, is lost in the higher symmetry group.

The data presented in Table I are for the homogeneous phase ($T > T_{SP}$), the crystal structure for $T < T_{SP}$ has yet to be determined in detail.

**Band structure** Based on the new crystal structure (Table I) we have calculated the energy bands of NaV$_2$O$_5$ within density functional theory (DFT). Thereby we have employed the full-potential linearized augmented plane wave code WIEN97. We have treated the exchange-correlation part by using the generalized gradient approximation. Also, local orbitals have been included for a better description of the semicore states (of Na-2s, Na-2p, V-3s, V-3p and O-1s).

The V-3d energy bands span a width of $\approx 5$ eV (see Fig. 2). The bottom of the 3d bands is separated by $\approx 3$ eV from the top of the O-2p band manifold. The sequence of 3d subband-splittings is in accordance with estimates by ligand field theory from recent $^{51}$V NMR data.

The four lowest-lying d bands predominantly exhibit V-d$_{xy}$ character (see Fig. 2). Actually, the d$_{xy}$ orbital planes are somewhat tilted around the b-axis towards the respective O(1) positions above or below the centers of the V-O-V rungs (see Fig. 3). The four d$_{xy}$ bands are split into two pairs of subbands, separated by $\approx 0.5–1$ eV. All bands exhibit significant dispersion along Γ-Y, to a lesser extend along Γ-X, but hardly any dispersion along Γ-Z.

Analysis of the DFT band states and mapping of the bands on those of tight-binding models yield the following result (model I): Bonding-type molecular orbital states, made up by the d$_{xy}$-orbitals of a V-O-V rung, coupled via the hopping term $t_{\|} \approx -0.38$ eV, form the lower pairs of subbands. Their dispersion along Γ-Y is produced by $t_{\|} \approx -0.17$ eV, their splitting at Γ, the small dispersion along Γ-X and the band-crossing along Γ-Y result from the small inter-ladder hoppings $t_1 \approx 0.012$ eV and $t_2 \approx 0.03$ eV (terms see Fig. 2 b)). The upper pair of subbands consists of the corresponding anti-bonding molecular orbitals.

In order to understand the microscopic origin of the effective hopping parameter $t_{\perp}$, $t_{01}$, $t_1$ and $t_2$, we have extended the tight-binding model by including the p$_x$ and p$_y$ orbitals of the basal plane O(1) and O(2) atoms (model II). We find strong contributions to $t_{\perp}$ and $t_{01}$ (of model I) by the indirect coupling of the V-d$_{xy}$ orbitals via the O-p, predominantly of p$^\pi$-type. Further contributions to $t_{\perp}$ and $t_{01}$ arise from residual three-center d-d terms involving the anionic oxygen potentials. The ratio $t_{\perp}/t_0 \approx 3.1$ is related to the tilt of the V-d$_{xy}$ orbitals, which reduces the V-d$_{xy} - O(2)$-p$_x$ coupling along b and increases the V-d$_{xy} - O(1)$-p$_y$ coupling. The residual direct d-d couplings are affected correspondingly by the tilt.

Further, the indirect contribution to $t_1$ via the V1-O(2)-V2 path is small due to a Goodenough-Kanamori-Anderson type interference effect in the (almost square-like) quadrangels of V1-O(2)-V2-O(2), which is similar to that discussed in CuGeO$_3$. The residual direct contributions to $t_1$ are affected by a compensation effect between two- and three-center contributions of opposite signs.

The sign of $t_{01}$ is derived from a symmetry analysis of the DFT eigenfunctions at the Γ-point. Admix-
Hartree-Fock approximation for our model I with on-site a shift of all V-d bands with respect to the O-p bands. In caused by the extra charge density $\Delta n$ fractional number of extra electrons. Though the doping value of $U$ by a DFT-calculation where we have doped a electron-electron interaction statements hold both in the cases of weak and of strong one gapless spin-excitation branch remains [19]. These tails will be discussed elsewhere.

Inclusion of other intra-ladder hopping parameters and not depend on the details of the tight-binding analysis. Correlation effects will lead to a charge gap and to $\Delta E = 0.14$ eV. We estimate $U \approx 2.8$ eV and a strong-coupling picture is therefore appropriate for NaV$_2$O$_5$. We may thus regard NaV$_2$O$_5$ as being built up from weakly coupled spin-1/2 chains with each spin located in a bonding V-O-V molecular wavefunction. Below $T_{SP}$ these chains of V-O-V spins dimerize and a spin-gap opens.

For $\Delta n = 0.1$ we find an energy shift $\Delta E = 0.14$ eV. We estimate $U \approx 2.8$ eV and a strong-coupling picture is therefore appropriate for NaV$_2$O$_5$. We may thus regard NaV$_2$O$_5$ as being built up from weakly coupled spin-1/2 chains with each spin located in a bonding V-O-V molecular wavefunction. Below $T_{SP}$ these chains of V-O-V spins dimerize and a spin-gap opens.

We now proceed to estimate the charge-transfer gap $E_c$ and the antiferromagnetic coupling $J_\parallel$. We neglect the inter-ladder couplings $t_1$ and $t_2$. Since $t_\perp \sim 3t_\parallel$ we may use perturbation-theory in $t_\parallel/t_\perp$. The one- and two-particle states of an isolated V-O-V rung are depicted in Fig. 4. The bonding and antibonding one-particle states have the energies $-t_\perp$ and $+t_\perp$ respectively. The exchange integral along a rung is $J_\perp \approx 4t_\perp^2/U \approx 0.41$ eV. In the ground state of the ladder all bonding states are filled and the first excited charge-transfer state is given by one empty and one doubly occupied rung with energy

$$E_c = 2t_\perp - J_\parallel \approx 0.71 \text{eV}.$$ 

This value for the charge-transfer agrees well with the 0.6 – 0.7 eV observed in optical absorption spectra [20]. The exchange coupling $J_\parallel$ between adjacent V-O-V molecular spins can be estimated by standard perturbation theory in $t_\parallel/t_\perp$ and is given by

$$J_\parallel = \frac{2t_\parallel^2}{E_c} \approx 80 \text{ meV},$$

which corresponds to 930 K. The exchange integral for NaV$_2$O$_5$ has been estimated to be 560-700 K [22]. DFT therefore overestimates $J_\parallel$ somewhat.

Outlook The above results indicate that $\alpha'$-NaV$_2$O$_5$ may be the first known quarter-filled ladder compound [5]. It is possible to dope charge carriers into the insulating quarter-filled state. One way is to introduce Na defects, Na$_8$V$_2$O$_5$, as the $\alpha'$-phase is stable for $0.7 < x < 1.0$ [23]. Alternatively one may consider the Ca substitution, Na$_{1-y}$Ca$_y$V$_2$O$_5$, since our results establish NaV$_2$O$_5$ and CaV$_2$O$_5$ to be isostructural [3] [4]. Varying $y \in [0, 1]$
would then allow to increase the carrier concentration continuously until a (highly anisotropic) half-filled ladder compound is obtained for \( y = 1 \). Note, that a spin-gap has been measured for CaV\(_2\)O\(_5\) \cite{24}.

**Conclusions** So far, \( \alpha' \)-NaV\(_2\)O\(_5\) has been considered as an inorganic spin-Peierls compound \cite{3}, where V\(^{+4}\) and V\(^{+5}\) ions are ordered in parallel chains \cite{2}. In this letter we present evidence that NaV\(_2\)O\(_5\) is in fact a quarter-filled ladder system, consisting of equivalent V atoms, and that NaV\(_2\)O\(_5\) is isostructural to CaV\(_2\)O\(_5\). Our results establish CaV\(_2\)O\(_5\) to be a half-filled ladder compound and thus explain the observed spin-gap in CaV\(_2\)O\(_5\). Our arguments are based on the crystallographic re-examination of NaV\(_2\)O\(_5\) by X-ray diffraction and energy-band calculations. We find the crystal structure to be centrosymmetric with only one equivalent V ion. This result does not allow for spontaneous charge disproportionation V\(^{+4}\) - V\(^{+5}\). A tight-binding analysis of the band structure leads to a one-dimensional Heisenberg model in the low-energy sector with a spin of 1/2 per rung of the ladder. These spins are not attached to a single V ion, but to a V-O-V molecular orbital. Our estimates for the charge-transfer gap and the exchange coupling agree with experiment.

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Note added in proof: A recent V-NMR study also finds \( \alpha' \)-NaV\(_2\)O\(_5\) = 1. Note, that a spin-gap above \( \alpha' \)-NaV\(_2\)O\(_5\) at \( T \approx 700 \) K \cite{29}. A recent analysis based on coupled chains finds J \( \approx 700 \) K \cite{29}.

\[ T_{SP} = 24, \text{ as does a crystal structure re-determination} \cite{29} \text{. The possibility of a molecular spin-state has also been discussed recently} \cite{29}. \]

| \( x \) | \( y \) | \( z \) | \( u(eq) \) |
|---|---|---|---|
| V | 4021(1) | 2500 | 3920(1) | 7(1) |
| Na | 2500 | -2500 | 8593(1) | 17(1) |
| O(1) | 2500 | 2500 | 5193(2) | 9(1) |
| O(2) | 1773(1) | 2500 | 4877(1) | 9(1) |
| O(3) | 2500 | 3954(1) | 578(1) | 15(1) |

**TABLE I.** Data collection parameters: NaV\(_2\)O\(_5\), Pmmm, compare Fig. 1. \( a=11.316(4) \) \( \AA \), \( b=3.611(1) \) \( \AA \), \( c=4.797(2) \) \( \AA \), \( z=2 \), \( T=293(2) \) \( \text{K} \), \( \lambda=0.6107 \), \( \sin \theta/\lambda_{\text{max}} = 1.365 \) \( \text{A}^{-1} \), full sphere, numerical absorption correction, \( R_{\text{int}} = 0.052 \), 2279 indep. data, 27 parameters, \( R_{p}=0.0238 \), \( wR^{2}=0.0483 \) for \( I > 2 \sigma(I) \).

**Atomic coordinates** \((\times 10^4)\) and equivalent isotropic displacement parameters \((A^2 \times 10^3)\), see Table above. The two additional O(2) depicted in Fig. 1 at \( (0.24, 0.75, 0.50) \) and \( (0.43, -0.25, 0.50) \) are generated by symmetry. Bond lengths \((\text{A})\): V-O(1): 1.8263(6), V-O(2): 1.9161(5) (2x), V-O(2): 1.9887(8) (1x), V-O(3): 1.6144(9), Na-O: 2.3533(9) (avg.), shortest V-V: 3.0400(7), shortest V-Na: 3.3537(8).

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