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Inversion Symmetry in the Spin-Peierls Compound α'-NaV$_2$O$_5$

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At room-temperature α'-NaV$_2$O$_5$ was found to have the centrosymmetric space group *Pmmn*. This space group implies the presence of only one kind of V site in contrast with previous reports [1] of the non-centrosymmetric counterpart *P2$_1$mn*. This indicates a non-integer valence state of vanadium. Furthermore, this symmetry has consequences for the interpretation of the transition at 34 K, which was ascribed to a spin-Peierls transition of one dimensional chains of V^{4+}.

I. COMMENT

Low dimensional quantum systems have revealed in recent years many new properties in their magnetic and electronic transport behavior. The vanadates complement in many respects the copper-oxide systems, with spin-less, S=0, 1/2 and 1 states, obtained by V^{5+} (d^0), V^{4+} (d^1), and V^{3+} (d^2), or Cu^{1+} (d^{10}), Cu^{2+} (d^9), and Cu^{3+} (d^8), respectively. Recently, the first observation of a spin-Peierls (SP) transition in an inorganic compound in CuGeO$_3$ [2] was complemented by the observation of a SP transition in α'-NaV$_2$O$_5$ [3]. Evidence for this one-dimensional magnetic behavior was found in the temperature dependence of the susceptibility, which can be accurately described at high temperatures by the Bonner-Fisher [4] model for a S=1/2 linear chain. Below T$_{SP}$=34 K an isotropic exponential decrease in the magnetic susceptibility is observed, as evidence for a non-magnetic ground state. The magnetic behavior of the SP state is complemented by SP signatures in a number of other measurements.

The usual interpretation of the transition at 34 K as SP transition is based on the structure determination of Carpy and Galy [1]. Their refinement, based on photographic data, in the non-centrosymmetric space group *P2$_1$mn*, allows for two vanadium positions in the asymmetric unit. These sites were interpreted with different valence states, V^{4+} and V^{5+}. In their model the resulting one dimensional S=1/2 V^{4+} chain can cause the observed Bonner-Fisher-like temperature dependence in the magnetic susceptibility, and a SP transition at low temperature. However, the reported structure determination of Carpy and Galy yielded atomic coordinates with a pseudo inversion center at (0.259, 0.25, 0.11) [5]. Therefore, we have undertaken a structure redetermination to investigate the (centro)symmetry.

The structure can be constructed from double-rows of edge sharing pyramids, one facing up and the other down. These double rows are connected by sharing corners, yielding a planar material. These planes are stacked with the Na in the channels of the pyramids, as shown in Fig. 1. The eight-fold coordination of Na is somewhat more symmetric with Na-O distances (2.4325(11)-2.6038(9) Å) than in the refinement of Carpy and Galy (2.43-2.90 Å) [1].

The α'-NaV$_2$O$_5$ structure it thus similar to that of CaV$_2$O$_5$ [6]. In CaV$_2$O$_5$ the V-O bond distances in the base of the square pyramids have a smaller range (1.90-1.98 Å *versus* 1.8259(6)-1.9867(9) Å). However, in this material the valence state of the V is uniformly 4+, making this material an interesting spin ladder-like compound.

We think that our structure determination is proof for the space group *Pmmn*. Our evidence is the very low R$_F$-value of 0.015, and the fact that no lower value of R$_F$ can be obtained when omitting the inversion center. The noncentrosymmetric space group *P2$_1$mn* reported by Carpy and Galy [1] is, in our opinion the result of the limited data set of 117 reflections, and the photographic-data quality.

Nevertheless it is worthwhile to assess the validity of very small distortions yielding lower symmetry. The centrosymmetric space group *Pmmn* indicates a non-integer valence of V, which contrasts with the observation of a SP transition and with the observed optical band gap of $\sim$1 eV. Therefore, we considered refinement in the polar 'equivalent' of *Pmmn*, *i.e.*, the non centrosymmetric space-group *P2$_1$mn*, in greater detail. This analysis shows that the standard deviations of the atomic positions in the polar refinement are approximately a factor ten larger than in the centrosymmetric refinement. This indicates much shallower minima in the least-squares refinement, caused by large correlation between atomic coordinates related by the pseudo-inversion-center. Similarly, the least-squares refinement protocol yields a substantial number (15) of large (> 0.90) correlation-coefficients between various parameters. Most equivalent bonds in *Pmmn* are in *P2$_1$mn* still almost equal. The largest difference in interatomic distances between formerly equivalent bonds is found for V-O1. The bond length of 1.8259(6) Å in *Pmmn* splits into 1.7966(63) Å and 1.8543(63) Å in *P2$_1$mn*, *i.e.*, a dis-

placement of 0.0289 Å from the average value of 1.8254. One can interpret this measure of noncentrosymmetry of 0.029 Å in two ways.

The common 'crystallographic' interpretation considers the noncentrosymmetry as an artifact. Table 2 shows that V and O's have all anisotropic temperature ellipsoids. It is well known that one can mimic this by making the space group noncentrosymmetric and using a more isotropic temperature factor. Obviously, this causes large correlation between parameters in the least-squares procedure. Furthermore, one should keep in mind that the calculated standard deviations are based on random fluctuations, and are significantly underestimated when correlation is important. Therefore, this interpretation assigns a much higher probability to the centric space group $Pmmn$.

An alternative interpretation is to use the statistics not to distinguish between the symmetries, but to quantify the maximum deviations from centrosymmetry in order to asses, $e.g.$, the magnitude of the transition dipole moment. Our analysis shows that the reported standard deviations for the atomic positions are based on the underlying symmetry. This allows 0.029 Å deviations from centrosymmetry, about five times larger than the calculated e.s.d. in the interatomic bond length, and should therefore be considered significant.

We conclude that our data are evidence for the centrosymmetric space group $Pmmn$. Deviations from centrosymmetry are unlikely but cannot be excluded up to 0.03 Å. The Flack x parameter is often used to indicate noncentrosymmetric structures. However, its value of 0.41(7) indicates at most twinning in case of a noncentrosymmetric structure, and this would still lead to a centrosymmetric 'space-average'.

While we have investigated the crystallographic structure of α'-NaV$_2$O$_5$, its electronic structure is not so obvious. Clearly, the original assignment of different valence states of V^{4+} and V^{5+} needs modification. Furthermore, the interpretation of the transition at 34 K as a SP transition requires a different model. Still, the 1-dimensional behavior of the magnetic susceptibility and the insulating properties of this non-integer valent material need to be incorporated in this theory. Also, the higher symmetry that we propose should be consistent with the symmetry as observed in, $e.g.$, Raman spectroscopy and IR spectroscopy. Further study of the electronic properties of α'-NaV$_2$O$_5$ is in progress.

II. EXPERIMENTAL

Crystal growth was carried out by the flux method by melting under vacuum appropriately compacted mixtures of V$_2$O$_5$, V$_2$O$_3$ and NaVO$_3$ in platinum crucibles and subsequently slow cooling of these melts from 1073

K to room temperature. Depending on the cooling parameters, either needle-shaped or plated shaped crystals, up to 2 cm long, were obtained [7].

For checking purpose we refined also in space group $P2_1mn$ which refinement converged to wR(F^2)=0.0512 for 1355 reflections with F$_0^2 \geq 0$ and 50 parameters and R(F)=0.0201 for 1245 reflections obeying F$_0 \geq 4.0$ σ(F$_0$). Inspection of the refined coordinates revealed a pseudo inversion center with the largest deviation for O1 of 0.03 Å [5,8]. The result of this refinement supports our result of the centro symmetric space group $Pmmn$.

The refinements are similar in the sense that V is coordinated by a square pyramid of O with the apical oxygen at smaller distance to V (1.6150(9) Å) than the ones at the base (1.8259(6)-1.9867(9) Å) $versus$ V1 1.622(4) and 1.854(6)-1.966(5), Carpy and Galy [1]: 1.65(5), 1.89(5)-1.96(5) Å and for V2 1.604(6), 1.800(6)-2.007(4)Å, Carpy and Galy [1]: 1.53(5), 1.76(5)-1.98(5) Å).

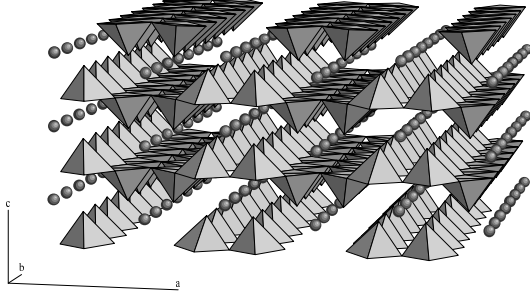| Crystal data	
α'-NaV$_2$O$_5$	D$_m$ not measured
M$_r$=204.87	Mo Kα radiation
Orthorhombic	λ=0.71073 Å
Pmmn	Cell param. from 22 refl.
a=11.311(1) Å	θ=14.57-22.37°
b=3.610(1) Å	μ=4.77 mm^{-1}
c=4.800(1) Å	T=295 K
V=196.00(7) Å^3	0.20x0.15x0.013 mm^3
Z=2	Black
D$_x$=3.471 Mg m^{-3}	Crystal source: synthesis
Data collection	
Enraf-Nonius CAD-4F diffract.	R$_{int}$=0.0232
$\omega/2\theta$ scans	θ_{max}=39.96°
Abs. corr.: gaussian by integr.	h=-20→20
T$_{min}$=0.6010; T$_{max}$=0.9381	k=0→6
1472 measured reflections	l= 0→8
701 independent reflections	frequency: 180 min
650 reflections with >2σ(I)	intensity decay: 1.0%
Refinement	
Refinement on F^2	$(\Delta/\sigma)_{max}$=0.001
R(F)=0.0151	$\Delta\rho_{max}$=0.675 e Å^{-3}
wR(F^2)=0.0386	$\Delta\rho_{min}$=-0.429 e Å^{-3}
S=1.126	Extinction corr.: SHELXL
701 reflections	Extinction coeff.: 0.067(4)
28 parameters	Scatt. factors: Cryst. Tab.

FIG. 1. Crystal structure of α'-NaV_2O_5; square pyramids around V (V-O1, V-O2, V-O3 x 3) and rows of Na.

V-01	1.8259(6)	V-O3^i	1.9156(6)
V-02	1.6150(9)	V-O3^{ii}	1.9867(9)
V-03	1.9156(6)		
O1-V-02	102.86(4)	O3-V-O3^i	140.87(3)
O1-V-03	92.15(2)	O3-V-O3^{ii}	77.74(2)
O1-V-03^i	92.15(2)	O3^i-V-O3^{ii}	77.74(2)
O1-V-03^{ii}	147.11(4)	V-O1-V^{iii}	140.89(6)
O2-V-03	108.42(2)	V-O3-V^{iv}	140.87(4)
O2-V-03^i	108.42(2)	V-O3-V^v	102.26(2)
O2-V-03^{ii}	110.03(4)	V^{iv}-O3-V^v	102.26(2)

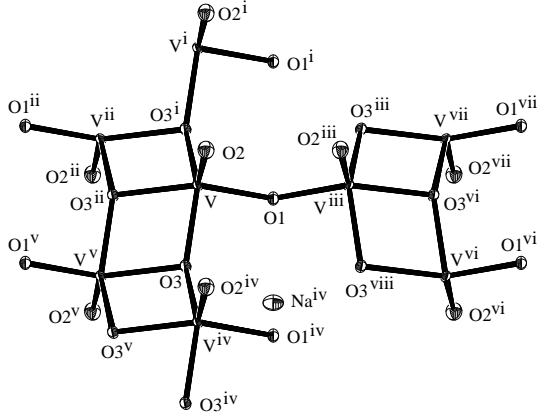TABLE II. Selected geometric parameters (Å, °).

FIG. 2. Drawing of NaV_2O_5 showing several VO_5 square pyramids, with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $x, 1+y, z$; (ii) $-x, \frac{1}{2}+y, 1-z$; (iii) $\frac{1}{2}-x, \frac{3}{2}-y, z$; (iv) $x, -1+y, z$; (v) $-x, -\frac{1}{2}+y, 1-z$; (vi) $\frac{1}{2}+x, 1-y, 1-z$; (vii) $\frac{1}{2}+x, \frac{1}{2}+y, 1+z$; (viii) $\frac{1}{2}-x, \frac{1}{2}-y, z$.]

[1] P.A. Carpy, and J. Galy, Acta Cryst. B **31**, 1481 (1975).
[2] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).
[3] M. Isobe, and Y. Ueda, J. Phys. Soc. Jpn. **65**, 1178 (1996).
[4] J.C. Bonner, and M.E. Fisher, Phys. Rev. A. **135**, 610 (1964).
[5] Y. La Page, J. Appl. Cryst. **20**, 264 (1987); J. Appl. Cryst. **21**, 983 (1988).
[6] M. Onada, and N. Nishiguchi, J. Solid State Chem. **127**, 359 (1996).
[7] M. Isobe, C. Kagami, and Y. Ueda, J. Crystal Growth **181**, 314 (1997).
[8] A.L. Spek, PLATON, Program for Data Reduction, Utrecth University, The Netherlands.

	x	y	z	U_{eq}
V	0.09788(1)	3/4	0.60781(30)	0.0073(1)
O1	1/4	3/4	0.4805 (20)	0.0094(2)
O2	0.11452(7)	3/4	0.94197(17)	0.0151(2)
O3	0.07302(6)	1/4	0.48769(16)	0.0097(1)
Na	1/4	1/4	0.14080(15)	0.0170(2)

TABLE I. Fractional atomic coordinates and equivalent isotropic parameters (Å^2).