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Inversion Symmetry in the Spin-Peierls Compound α'-NaV2O5

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Abstract

At room temperature, sodium pentaoxodivanadate, NaV_2O_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 [Carpy & Galy (1975). *Acta Cryst.* **B31**, 1481–1483] of the non-centrosymmetric $P2_1mn$ counterpart. 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+} ions.

Comment

In recent years, low-dimensional quantum systems have revealed many new properties in their magnetic and electronic transport behavior. In many respects, the vanadates complement the copper oxide systems, with spinless $S = 0$, $\frac{1}{2}$ and 1 states, obtained by V^{5+} (d^0), V^{4+} (d^1) and V^{3+} (d^2), or Cu^+ (d^{10}), Cu^{2+} (d^9) and Cu^{3+} (d^8), respectively. Recently, the first observation (Hase *et al.*, 1993) of a spin-Peierls (SP) transition in an inorganic compound, $CuGeO_3$, was complemented by the observation (Isobe & Ueda, 1996) of an SP transition in NaV_2O_5. 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 (Bonner & Fisher, 1964) model for an $S = \frac{1}{2}$ linear chain. Below $T_{SP} = 34$ K, an isotropic exponential decrease in the magnetic susceptibility is observed, evidence for a nonmagnetic 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 a spin-Peierls transition is based on the structure determination of Carpy & Galy (1975). Their refinement, based on photographic data, in the non-centrosymmetric space group $P2_1mn$, allows for two V-atom positions in the asymmetric unit. These sites were interpreted with different valence states, *i.e.* V^{4+} and V^{5+}. In their model, the resulting one-dimensional $S = \frac{1}{2}$ V^{4+} chain can cause the observed Bonner–Fisher-like temperature dependence in the magnetic susceptibility, and a spin-Peierls transition at low temperature. However, the reported structure determination of Carpy & Galy (1975) yielded atomic coordinates with a pseudo-inversion center at (0.259,0.25,0.11) (Le Page, 1987, 1988). 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 pyramid corner-sharing, yielding a planar material. These planes are stacked with the Na^+ ions in the channels of the pyramids, as shown in Fig. 1. The eightfold coordination of sodium is somewhat more symmetric [with Na—O distances of 2.4325(11)–2.6038(9) Å] than in the refinement of Carpy & Galy (1975) (Na—O 2.43–2.90 Å). The structure of NaV_2O_5 it thus similar to that

of CaV_2O_5 (Onada & Nishiguchi, 1996). In CaV_2O_5, the V—O bond distances in the base of the square pyramids have a smaller range [1.90–1.98 *versus* 1.8259 (6)–1.9867 (9) Å]. However, in this material, the valence state of vanadium is uniformly 4+, making this material an interesting spin ladder-like compound.
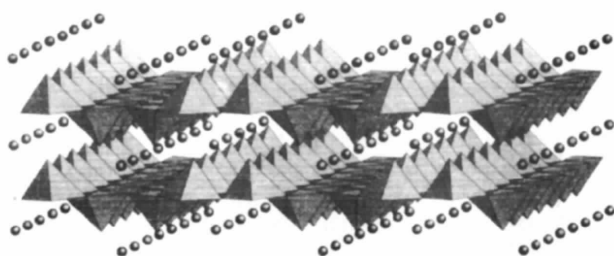

Fig. 1. A view of the crystal structure of NaV_2O_5 showing square pyramids around V (V–O1, V–O2, V–O3 × 3) and rows of Na atoms.

We believe that our structure determination provides 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 non-centrosymmetric space group $P2_1mn$ reported by Carpy & Galy (1975) is, in our opinion, the result of the limited data set (117 reflections) and the quality of the photographic data. Nevertheless, it is worthwhile assessing the validity of very small distortions yielding lower symmetry. The centrosymmetric space group *Pmmn* indicates a non-integer valency of V, which contrasts with the observation of a spin-Peierls transition and with the observed optical bandgap of ∼1 eV. Therefore, we considered refinement in the polar 'equivalent' of *Pmmn*, *i.e.* the non-centrosymmetric space group $P2_1mn$, in greater detail. This analysis shows that the standard deviations of the atomic positions in the polar refinement are approximately a factor of 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 $P2_1mn$ 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 1.797 (6) and 1.854 (6) Å in $P2_1mn$, *i.e.* a displacement of 0.0289 Å from the average value of 1.8254 Å. One can interpret this measure of non-centrosymmetry of 0.029 Å in two ways. The common 'crystallographic' interpretation considers the non-centrosymmetry as an

artefact. All V and O atoms have anisotropic displacement ellipsoids. It is well known that one can mimic this by making the space group non-centrosymmetric and using a more isotropic displacement parameter. 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 centrosymmetric 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 assess, for example, 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.'s in the interatomic bond lengths, 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 (1983) x parameter is often used to indicate non-centrosymmetric structures. However, its value of 0.41 (7) indicates, at most, twinning in the case of a non-centrosymmetric structure, and this would still lead to a centrosymmetric 'space average'.

While we have investigated the crystallographic structure of NaV_2O_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,
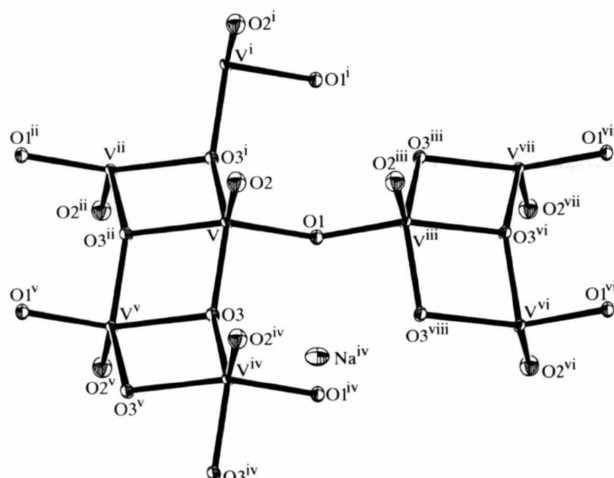

Fig. 2. Drawing of NaV_2O_5 showing several VO_5 square pyramids, with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) x, $1 + y$, z; (ii) $-x$, $\frac{1}{2} + y$, $1 - z$; (iii) $\frac{1}{2} - x$, $\frac{3}{2} - y$, z; (iv) x, $-1 + y$, z; (v) $-x$, $-\frac{1}{2} + y$, $1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

the interpretation of the transition at 34 K as a spin-Peierls transition requires a different model. Still, the one-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, for example, Raman and IR spectroscopy. Further study of the electronic properties of NaV$_2$O$_5$ is in progress.

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 (Isobe & Ueda, 1998).

Crystal data

NaV$_2$O$_5$	Mo $K\alpha$ radiation
$M_r = 204.87$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 22
$Pmmn$	reflections
$a = 11.311\,(1)$ Å	$\theta = 14.57$–$22.37°$
$b = 3.610\,(1)$ Å	$\mu = 4.77$ mm^{-1}
$c = 4.800\,(1)$ Å	$T = 295$ K
$V = 196.00\,(7)$ Å^3	Rectangular plate
$Z = 2$	$0.20 \times 0.15 \times 0.013$ mm
$D_x = 3.471$ Mg m^{-3}	Black
D_m not measured	

Data collection

Enraf–Nonius CAD-4F diffractometer	650 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.023$
Absorption correction:	$\theta_{max} = 39.96°$
Gaussian by integration	$h = -20 \rightarrow 20$
(Spek, 1983)	$k = 0 \rightarrow 6$
$T_{min} = 0.601$, $T_{max} = 0.938$	$l = 0 \rightarrow 8$
1472 measured reflections	3 standard reflections
701 independent reflections	frequency: 180 min
	intensity decay: 1.0%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.675$ e Å^{-3}
$R(F) = 0.015$	$\Delta\rho_{min} = -0.429$ e Å^{-3}
$wR(F^2) = 0.039$	Extinction correction:
$S = 1.126$	SHELXL97 (Sheldrick,
701 reflections	1997b)
28 parameters	Extinction coefficient:
$w = 1/[\sigma^2(F_o^2) + (0.0189P)^2]$	0.067 (4)
where $P = (F_o^2 + 2F_c^2)/3$	Scattering factors from
$(\Delta/\sigma)_{max} = 0.001$	International Tables for Crystallography (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
V	0.09788 (1)	3/4	0.60781 (3)	0.0073 (1)
O1	1/4	3/4	0.4805 (2)	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 2. *Selected geometric parameters (Å, °)*

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

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) $x, y - 1, z$; (v) $-x, y - \frac{1}{2}, 1 - z$.

For checking purposes, we also refined in space group $P2_1mn$; this refinement converged at $wR(F^2) = 0.0512$ for 1355 reflections with $F_o^2 \geq 0$ and 50 parameters, and $R(F) = 0.0201$ for 1245 reflections obeying $F_o \geq 4\sigma(F_o)$. Inspection of the refined coordinates revealed a pseudo-inversion center with the largest deviation of 0.03 Å for O1 (Le Page, 1987, 1988; Spek, 1996). The result of this refinement supports our adoption of the centrosymmetric space group $Pmmn$. The refinements are similar in the sense that vanadium is coordinated by a square pyramid of O atoms with the apical O atom at a shorter distance from V than the O atoms of the base [V—O$_{apical}$ 1.6150 (9) Å and V—O$_{basal}$ 1.8259 (6)–1.9867 (9) Å for $Pmmn$; cf. V1—O$_{apical}$ 1.622 (4) Å and V1—O$_{basal}$ 1.854 (6)–1.966 (5) Å for $P2_1mn$, and 1.65 (5) and 1.89 (5)–1.96 (5) Å, respectively, according to Carpy & Galy (1975), and V2—O$_{apical}$ 1.604 (6) and V2—O$_{basal}$ 1.800 (6)–2.007 (4) Å for $P2_1mn$, and 1.53 (5) and 1.76 (5)–1.98 (5) Å, respectively, according to Carpy & Galy (1975)].

Data collection: *CAD-4-UNIX Software* (Enraf–Nonius, 1994). Cell refinement: *SET4* (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *CaRine* (Boudias & Monceau, 1996), *ORTEP* (Johnson, 1965) and *PLATON* (Spek, 1994, 1996). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Cobalt Lithium Orthoborate, LiCoBO₃

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Abstract

The title compound has been synthesized by a solid state reaction. Its structure is isotypic with those o LiMgBO₃, LiMnBO₃ and LiZnBO₃. Co^{II} occupies sta. tistically two close positions within the CoO₅ trigo. nal bipyramids. These polyhedra share edges to form chains running along the [$\bar{1}$01] axis and are linked together, *via* corner sharing, by BO₃ planar groups. The Li atoms occupy statistically the center of two face-sharing tetrahedra. Such pairs of tetrahedra share edges to form chains running along the *c* axis.

Comment

Several M^{II} lithium orthoborates, LiM^{II}BO₃, have already been identified for *M* = Mg, Mn, Co, Zn and

Cd. For some of them, single-crystal structure determinations have been reported, allowing the identification of three structure types. However, other types of cells have also been proposed on the basis of powder data. The overall structural information can be summarized as follows:

(i) LiMgBO₃ (Norrestam, 1989), LiZnBO₃ and LiMnBO₃ (Bondareva *et al.*, 1978) exhibit isotypic monoclinic structures (*C*2/*c* space group).

(ii) LiCdBO₃ crystallizes in three forms, two of which are clearly established, *i.e.* LiCdBO₃-I, with a triclinic structure (*P*$\bar{1}$ space group; Sokolova *et al.*, 1979), and a hexagonal form (*P*$\bar{6}$ space group) for LiCdBO₃-II (Kasanskaja *et al.*, 1978; Sokolova *et al.*, 1980). A third form, with a monoclinic cell, has been proposed (Wei *et al.*, 1990), but the structure is not yet known.

(iii) A new monoclinic form of LiZnBO₃ has recently been identified (Belkébir *et al.*, 1996) and on account of the cell parameters, its structure is very likely to be a more symmetrical version of the LiCdBO₃-I triclinic form mentioned above.

(iv) Based on X-ray powder data, a monoclinic cell and the *P*2₁/*c* space group have recently been proposed for LiMgBO₃ (Belkébir *et al.*, 1996), however, all the lines of the powder pattern are also compatible with the *A*2/*a* space group (*C*2/*c* if one inverts the *a* and *c* parameters) and, accordingly, the structure of this compound is very likely to be that already mentioned above (Norrestam, 1989). Similarly, all lines [except a weak one, ($\bar{3}$43)] of the powder pattern of LiCoBO₃ (Belkébir *et al.*, 1996) are also compatible with the *A*2/*a* space group and the present paper shows that the crystal structure of this compound is isotypic with those of LiMgBO₃, LiZnBO₃ and LiMnBO₃.

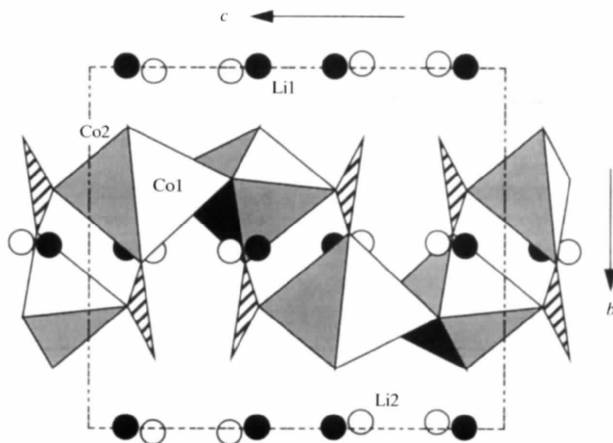In LiCoBO₃, the Co^{II} cation occupies statistically two close positions [Co1–Co2 0.199 (4) Å] within the

Fig. 1. View of the title structure along [100] showing edge-sharing CoO₅ trigonal bipyramids (shaded), triangular BO₃ groups (dashed), and pairs of Li1 (black circles) and Li2 (open circles) sites (half occupied).