

A High-Pressure Form of Lithium Vanadium Dioxide – a $2 \times 2 \times 2$ NaCl Superstructure

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Abstract

A high-pressure form of LiVO_2 was prepared by treating the ambient-pressure phase at 6.0–6.5 GPa and 1300 K. This metastable product, which has retained its structure over the past ten years, was studied with precession and Weissenberg methods. A complete structural study was then carried out utilizing a four-circle diffractometer on two distinct crystals. The high-pressure phase was found to possess the cubic space group $Fd\bar{3}m$ with $a = 8.227(2) \text{ \AA}$ and $Z = 16$. The structure was refined from the two sets of reflections with $2\theta (\text{Mo } K\alpha) \leq 100^\circ$. The R and R_w were 0.072 and 0.028, respectively, using $w = 1/\sigma_F^2$ (for 136 reflections with measurable intensity). The structure is a $2 \times 2 \times 2$ NaCl superstructure with partial or short-range ordering of Li and V atoms occupying the octahedral interstices formed by the close-packed O atoms. The O array is distorted slightly, 0.02 Å from an F -lattice complex. If layers perpendicular to a $[111]$ direction are represented by the dominant atoms with their relative positions labelled by A , B , and C as subscripts, the stacking sequence is $O_A M_A O_B m_B O_C M_C O_A m_A O_B M_B O_C m_C$, where M and m are two types of metal-atom layers.

Introduction

The ternary oxide LiVO_2 is of great interest to solid-state scientists because of its unusual electrical and magnetic transition at approximately 560 K (Kobayashi, Kosuge & Kachi, 1969). At this temperature, there is a discontinuity in unit-cell parameters. Several investigations have been carried out on powders of this interesting compound (Bongers, 1975; Reuter, Weber & Jaskowsky, 1962). In an attempt to prepare single crystals for structural study, we treated the LiVO_2 powder in a high-temperature/high-pressure anvil device. This experiment did not result in the

formation of single crystals of the rhombohedral phase, but single crystals of a metastable high-pressure phase were obtained instead. We now report the structure of this phase.

Experimental

Conversion of α - LiVO_2 into cubic LiVO_2

The ambient-pressure phase, α - LiVO_2 , was prepared by two chemical methods. The first is by the hydrothermal reaction of LiOH with VO at 1000 K and 0.3 GPa for 8 h. The water medium in this case acts as a buffered oxidizing agent to yield LiVO_2 in the form of a black powder. The powder diffraction pattern of this product could be indexed on a hexagonal cell, and the refinement gave $a = 2.844(1)$ and $c = 14.763(2) \text{ \AA}$. However, the lattice is rhombohedral and the above data indicate a primitive unit cell with $a = 5.188 \text{ \AA}$ and $\alpha = 31^\circ 49'$. The hexagonal cell parameters compare well with those ($a = 2.84$ and $c = 14.7 \text{ kX}$) given by Rüdorff & Becker (1954). The second preparative method involved the solid-state reaction and reduction of Li_2CO_3 with V_2O_5 at 770 K in H_2/Ar (20/80) for 12 h. For this product, the a and c parameters were 2.838(2) and 14.803(3) Å respectively. Since the powder data are not in the JCPDS file, these are presented in Table 1.

Table 1. Powder diffraction data for α - LiVO_2

Radiation: $\text{Cu } K\alpha$; intensity: densitometer reading; hexagonal unit-cell parameters: $a = 2.838(2)$, $c = 14.803(3) \text{ \AA}$.

hkl	$d(\text{obs.})$	$d(\text{calc.})$	$I(\text{obs.})$	hkl	$d(\text{obs.})$	$d(\text{calc.})$	$I(\text{obs.})$
0 0 3	4.935	4.934	95	0 0 0	1.645	1.645	5
0 0 6	2.467	2.467	10	1 0 7	1.603	1.603	25
1 0 1	2.425	2.424	70	0 1 8	1.478	1.478	40
0 1 2	2.332	2.332	20	1 1 0	1.419	1.419	40
1 0 4	2.047	2.047	100	1 1 3	1.364	1.364	20
0 1 5	1.891	1.891	30	1 0 10	1.268	1.268	5

Table 2. Powder diffraction data for high-pressure LiVO_2

Radiation: Cu $K\alpha$; intensity: visual estimate; $a_0 = 8.210(4) \text{ \AA}$.

<i>hkl</i>	<i>d</i> (obs.)	<i>d</i> (calc.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (obs.)	<i>d</i> (calc.)	<i>I</i> (obs.)
1 1 1	4.844	4.740	strong	6 0 0	1.372	1.368	weak
3 1 1	2.440	2.475	medium	5 3 3	1.250	1.252	weak
2 2 2	2.366	2.370	weak	6 2 2	1.237	1.238	v. weak
4 0 0	2.047	2.052	v. strong	4 4 4	1.185	1.185	medium
3 3 1	1.890	1.883	medium	7 1 0	1.160	1.161	v. weak
5 1 1	1.594	1.580	medium	8 0 0	1.027	1.026	v. weak
4 4 0	1.449	1.451	medium				

The transformation of the ambient-pressure phase was carried out in a tetrahedral anvil or belt-type anvil system at 6.0–6.5 GPa pressure. The pressure was first applied then the temperature was increased to that desired (1300 K) in all experiments. After one hour under the given reaction conditions, the sample was quenched to room temperature and the pressure was slowly released yielding the cubic product. The experiments were carried out in gold capsules to maintain the proper O stoichiometry in the product.

The powder pattern of the high-pressure cubic phase is given in Table 2. The crystallographic data were obtained in a Debye–Scherrer camera utilizing properly filtered Cu $K\alpha$ or Cr $K\alpha$ radiation. The unit-cell parameter was calculated with a least-squares computer program ($a = 8.210 \pm 4 \text{ \AA}$).

The crystals have a charcoal-black appearance and cleave into tetragonal rods. These rods can be further cut with a razor blade into small cubes.

The thermal treatment of the high-pressure phase showed a weak endotherm at 703 K, and on return to room temperature exhibited a reversible transformation at $448 \pm 10 \text{ K}$. This thermal treatment was shown to yield the ambient-pressure phase by its powder diffraction pattern indexed with $a = 2.846 \pm 1$ and $c = 14.767 \pm 3 \text{ \AA}$.

The cubic LiVO_2 phase was found to be a semiconductor possessing a band-gap activation energy of 0.14 eV. The magnetic data showed Curie–Weiss behaviour from 100 to 300 K. Calculations gave a paramagnetic Weiss constant of $\sim 390 \text{ K}$ and an effective magnetic moment of $18.3 \times 10^{-24} \text{ J T}^{-1}$. No field dependence was observed at 77 K.

Single-crystal study of cubic LiVO_2

Rotation, Weissenberg, and precession photographs on single crystals of the high-pressure LiVO_2 indicated a cubic F -type lattice with $a = 8.23 \text{ \AA}$. Two crystals, cubes with edges $\sim 0.2 \text{ mm}$, were then selected and mounted on a Syntex $P2_1$ diffractometer on which a data set was collected from each. The cell dimension and orientation matrix were refined by the least-squares method from the angles of 11 reflections automatically measured by the diffractometer in both cases. The density was obtained by a pycnometric experiment.

Crystal data

LiVO_2 , space group $Fd3m$, $a = 8.227(2) \text{ \AA}$, $V = 556.8(4) \text{ \AA}^3$; $D_o = 4.23(7)$ and $D_x = 4.288 \text{ Mg m}^{-3}$ with $Z = 16$; $\mu(\text{Mo } K\alpha) = 6.90 \text{ mm}^{-1}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$.

For both crystals, 173 independent reflections with $2\theta \leq 100^\circ$ were measured using θ – 2θ scan methods. The scan speed varied from $0.5^\circ \text{ min}^{-1}$ for weak to $29.3^\circ \text{ min}^{-1}$ for strong reflections. For crystals (I) and (II), 136 (79%) and 127 (73%) reflections respectively have measurable intensity and were all included in the structural analysis. Structure amplitudes were derived by applying the Lorentz and polarization corrections. No absorption correction was made, $\mu R \leq 1.19$.

Derivation of the structure

Our preliminary crystallographic results indicated a NaCl-type structure having a doubled unit-cell edge. Previous theoretical analyses of the NaCl structure by Brunel, De Bergevin & Gondrand (1972) indicated a possible arrangement of two metals in an F -lattice complex of oxygen possessing a structure with space group $Fd3m$. No chemical was then known with this particular structure.

Refinement of the structure

A least-squares refinement with the ordered NaCl structure was used as a model. The positional parameter for the O, three temperature factors, and the scale factor were varied using a highly modified version of *ORFLS* (Busing, Martin & Levy, 1962). An R ($= \sum |F_o| - |F_c| / \sum |F_o|$) of 0.41 was obtained when the temperature factors for Li and V were assumed to be the same. The peaks for Li on the Fourier map calculated at this stage were larger than those of O and slightly smaller than those of V. Since the octahedral ionic radii for Li^+ and V^{3+} are similar (0.74 vs 0.64 \AA), a model involving disorder between the two metal sites was tested. Multiplicity factors of the metal atoms were then allowed to vary while other parameters were fixed from a previous cycle. Further refinements gave the distributions listed in Table 3. At the final stage of refinement, composite atomic scattering factors were taken from Cromer & Waber (1965) for $(\frac{1}{3}\text{Li} + \frac{2}{3}\text{V})$ and $(\frac{2}{3}\text{Li} + \frac{1}{3}\text{V})$. No distribution would give equal temperature parameters for both metal sites. With $\frac{1}{3}\text{Li} + \frac{2}{3}\text{V}$ in both metal sites, *i.e.* a completely random distribution, the R value was 0.13. With $\frac{2}{3}\text{Li} + \frac{1}{3}\text{V}$ in 16(a) and $\frac{1}{3}\text{Li} + \frac{2}{3}\text{V}$ in 16(c), the R factor was 0.11. Under the same conditions, the distribution of metal atoms given in Table 3 yielded an R of 0.086. At that stage, the multiplicity factors did not vary significantly. Refinements from both sets of intensities gave the same distribution. A weighting function based on the estimated standard deviation, $w = 1/\sigma^2(F)$, was

Table 3. Final structure compared with the NaCl superstructure

Site sets*	LiVO ₂			NaCl superstructure	
	Atom	Coordinates	B (Å ²)†	Atom	Coordinates
16(c)	$\frac{2}{3}$ V + $\frac{1}{3}$ Li	$\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$	1.13 (5)	M	$\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$
16(d)	$\frac{1}{3}$ V + $\frac{2}{3}$ Li	$\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$	1.4 (1)	M	$\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$
32(c)	O	-0.1236 (5), † -0.1236, -0.1236	1.12 (4)	X	-0.125, -0.125, -0.125

* Space group $Fd\bar{3}m$, origin at $\bar{4}3m$.

† For crystal (II), $x = -0.1220$ (4). Temperature parameters of 16(c), 16(d), and 32(c) are 1.02 (4), 1.6 (1), and 1.15 (4) Å², respectively.

then used and the final R and R_w [$= \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$] were 0.072 and 0.028 respectively for crystal (I), and 0.081 and 0.019 respectively for crystal (II). Final atomic parameters are given in Table 3.*

Results and discussion

The structure of the high-pressure LiVO₂ phase can be regarded as a $2 \times 2 \times 2$ NaCl superstructure (Fig. 1) with two features: (i) The structure is partially disordered, $\frac{1}{3}$ Li + $\frac{2}{3}$ V rather than all V in 16(c) (m in Fig. 2), and $\frac{2}{3}$ Li + $\frac{1}{3}$ V rather than pure Li in 16(d) (M in Fig. 2). It is not known whether the disorder is a result of fine-scale twinning of short-range-order crystals or genuine disorder. It was noticed that on X-ray photographs all the reflections due to the superstructure are diffuse (not just weak), in contrast to the sharp reflections that could be indexed on a NaCl-type structure. Thus it is possible that the crystal has only short-range order, and further work is underway using electron microscopy to clarify this point. (ii) The positions of O atoms deviate from the F -lattice complex by 0.02 Å. As a result, the O atoms are closer (0.04 Å) to one type of $\bar{4}3m$ centre, which is designated as T and \bar{T} , than the other type T' and \bar{T}' (see Fig. 2). Centres \bar{T} and \bar{T}' are related to T and T' respectively *via* centres of symmetry. This type of distortion is easily described in terms of two geometric units (Chieh, 1979, 1980): $O_{4m_{0.5 \times 4}}$ and $M_{0.5 \times 4}$. The O atoms can be grouped into tetrahedra for reasons given in Chieh (1980), but the most important point to note in this discussion is the tetrahedral arrangement of the m and M ions, which are embedded in a tetrahedrally distorted cubic closest packing of the O atoms.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36119 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

α -LiVO₂ has a rhombohedral NaCl superstructure similar to that given for LiNiO₂ (Wells, 1975, p. 219). The O atoms form a slightly distorted ($\alpha = 31^\circ 49'$ instead of 33.56°) c.c.p. array with alternate layers of Li and V atoms in the [111] direction, occupying all the octahedral interstices. In the high-pressure phase, the f.c.c. array of O atoms is distorted in a different fashion as described above, and both m and M are present in layers parallel to the (111) plane. There are two types of metal-atom layers, one dominated by M and the other by m . Stacking of these layers is shown in Fig. 3, in which the O atoms are completely ignored. If layers are represented by the dominant metal atoms with their relative positions in space labelled by A , B , and C as subscripts, the stacking sequence is $O_A M_A O_B m_B$.

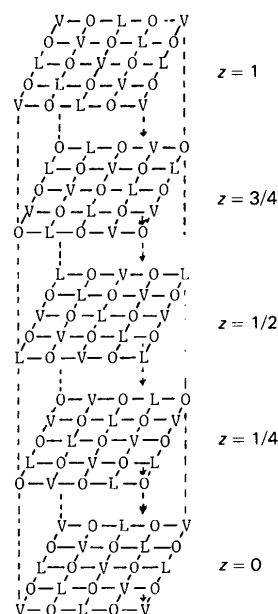


Fig. 1. The proposed arrangement of atoms in a $2 \times 2 \times 2$ NaCl superstructure of LiVO₂.

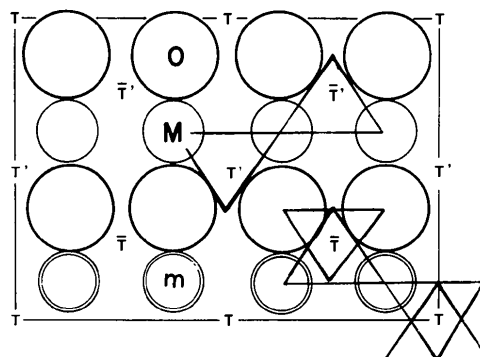


Fig. 2. The atoms and tetrahedra on a (110) plane. T , \bar{T} , T' and \bar{T}' are centres of $\bar{4}3m$ symmetry in $Fd\bar{3}m$ with \bar{T} and \bar{T}' being the inverse of T and T' , respectively; $m = \frac{1}{3}$ Li + $\frac{2}{3}$ V and $M = \frac{2}{3}$ Li + $\frac{1}{3}$ V.

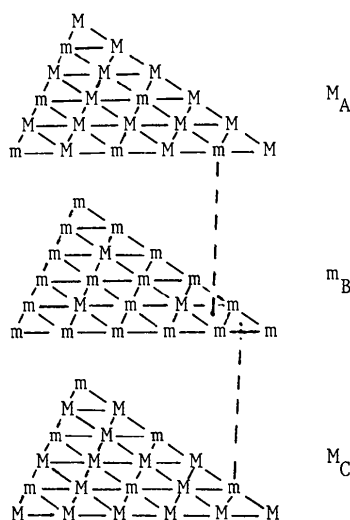


Fig. 3. Packing of metal atoms M and m viewed as layers in a $[111]$ direction.

$O_C M_C O_A \dots$. The site symmetry of the O atom is $\bar{3}2/m$ in both the α and the high-pressure forms of LiVO_2 .

A theoretical treatment (Brunel *et al.*, 1972) suggested a structure for an ordered $2 \times 2 \times 2$ superstructure of NaCl having the formula ABX_2 , and the first example to be discovered was the sulphide LiTbS_2 , by Plug & Prodan (1978) using electron microscopy; this structure, however, exists only in short-range order. A similar order cannot be ruled out for crystals of cubic LiVO_2 as indicated previously. Two recent surveys

(Hauck, 1980; Chieh, 1980) do not report any ordered structure of this type. In a short-range-ordered structure, Li and V may occupy the positions of M and m respectively.

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Structure du Sulfure de Cuivre et de Silicium Cu_8SiS_6

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Abstract

Cu_8SiS_6 crystallizes in the orthorhombic system, space group $Pmn2_1$, with $a_o = 6.9928$ (6), $b_o = 6.9000$ (13), $c_o = 9.7723$ (14) Å, and $Z = 2$, $d_m = 5.05$ (6), $d_x = 5.15 \text{ Mg m}^{-3}$. The structure was refined to a final R index of 0.031 with 205 independent reflections (Mo $K\alpha$, $\mu = 19.7 \text{ mm}^{-1}$). Cu_8SiS_6 is isotypic with $\text{Ag}_8\text{GeSe}_6(\beta')$.

Introduction

Des composés de formule $M_8M'X_6$ ont été mis en évidence dans un certain nombre de systèmes. Rysanek, Laruelle & Katty (1976) ont déterminé la structure de Ag_8GeTe_6 , Krebs & Mandt (1977), celle de Ag_8SiS_6 isotype de Ag_8GeS_6 (Eulenberger, 1977). Kuhs, Nitsche & Scheunemann (1978) ont retrouvé ce même type de structure dans $\text{Cu}_6\text{PS}_5\text{Br}$ ainsi que Carré, Ollitrault-