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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the
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Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals ñ it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

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Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

	Experiment title: Magic number ordering in layered lithium vanadates	**Experiment number**: CH-1420
Beamline: BM01B	**Date of experiment**: from: 11/12/02 to: 14/12/02	**Date of report**: 22/01/04
Shifts: 9	**Local contact(s)**: Wouter Van Beek	*Received at ESRF:*

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Report:

Low-dimensional spin systems with s = Ω and a singlet ground state are of interest because of their fundamental quantum nature. These systems have been discovered mainly in copper and nickel compounds, [1, 2] however, since the discovery of spin-gap in CaV_4O_9 [3] (the first realisation of a two-dimensional spin-plaquette system), more attention has been focused on low-dimensional magnetic systems with s = Ω V^{4+} ions. The potential analogy between d^1 (s = Ω) and d^9 (s = Ω) high temperature superconductors also makes these systems of interest. Compounds of the vanadate family containing VO_5 square pyramids are examples of such systems; vanadium ternary oxides and bronzes with unfilled $3d$ orbitals often have phase transitions from paramagnetic to spin-singlet states [4] as seen, for example in the quasi-one-dimensional β-$Na_xV_2O_5$ ($x \approx {}^1/_3$), which exhibits a kind of charge-density-wave associated with a V^{4+}-V^{4+} bonded pair [5].
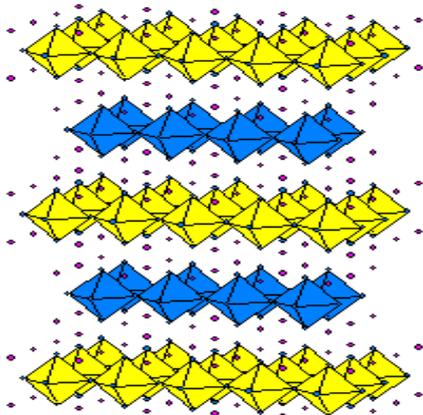
Figure 1 - LaSrNiO₄ showing ì charge stripesî of Ni^{2+} and Ni^{3+}

We were allocated time on beam line BM01B to study compounds with the general formula $Li_xV_2O_5$. The system can adopt many structural phases depending on temperature and lithium concentration, *x*, as well as the method of preparation. The amount of lithium intercalated into these compounds was selected to promote charge ordering ñ the localisation of different oxidation states onto crystallographically distinct sites within a single compound ñ within the crystal structures. In seriesí such as $La_{2-x}Sr_xNiO_4$, an arrangement of charge stripes was observed with certain ìmagicî values of *x* that produce the correct ratio of Ni^{2+}:Ni^{3+}, in other words, an integer ratio of d^0:d^1 ions is observed where charge ordering occurs i.e. *x* = 0.25, 0.5, 0.66, 1Ö ñ the ìmagic numbersî. We controlled the ratio of magnetic to non-magnetic ions with the aim of producing crystal structures containing chains of magnetic (d^1) $V^{4+}O_5$ square pyramids separated by chains of non-magnetic (d^0) $V^{5+}O_5$ square pyramids i.e. a low-dimensional magnetic system.

High quality x-ray diffraction data were essential to complement neutron diffraction experiments previously carried out and allow full structural characterisation. Data were collected on eight samples with various compositions over a range of temperatures from 15-300K. Lithium vanadates have a layered structure, shown in figure 2. At room temperature there is an increase in strain and distortion in the layers of VO_5 square

pyramids, measured by the puckering angle, μ, as the lithium content increases, up to a boundary composition where a phase transition occurs allowing coordination of lithium in a different site and a decrease in distortion of the V_2O_5 layers (figure 3). It seems that when the lithium content is low, it is energetically favourable to have a relatively unstable lithium site within less distorted host lattice layers; as the lithium content increases, there comes a point when the distortions in the host lattice are outweighed by the stability of the lithium site and the structure is thus driven ultimately towards a layer shift enabling more stable coordination of lithium. The intercalation of lithium into this system therefore has an implicit strain effect for the host lattice layers.
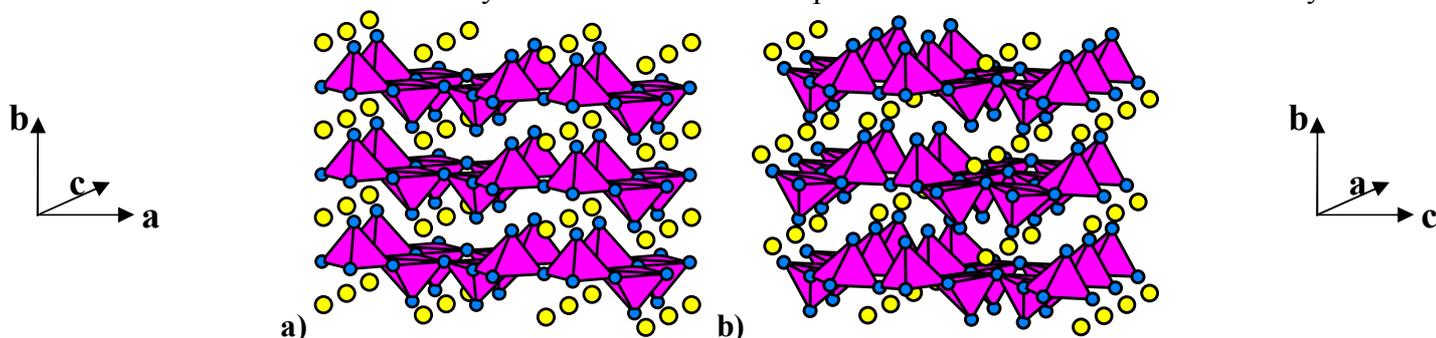

Figure 2 ñ Structures of a) α-Li$_{0.13}$V$_2$O$_5$ and b) δ-Li$_{0.95}$V$_2$O$_5$ from refined diffraction data.
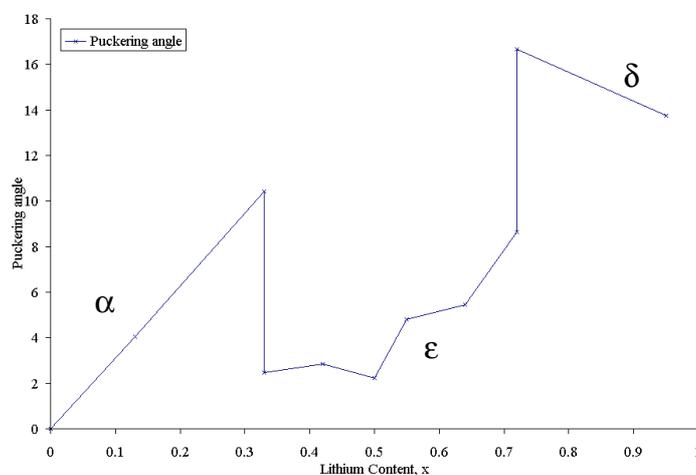

Figure 3 ñ Variation of puckering angle with lithium content.

Refinement of high resolution x-ray diffraction data not only allowed elucidation of the main structure for each composition, but also showed the presence of extra, much weaker peaks for certain compositions and temperatures (see figures 4 and 5).
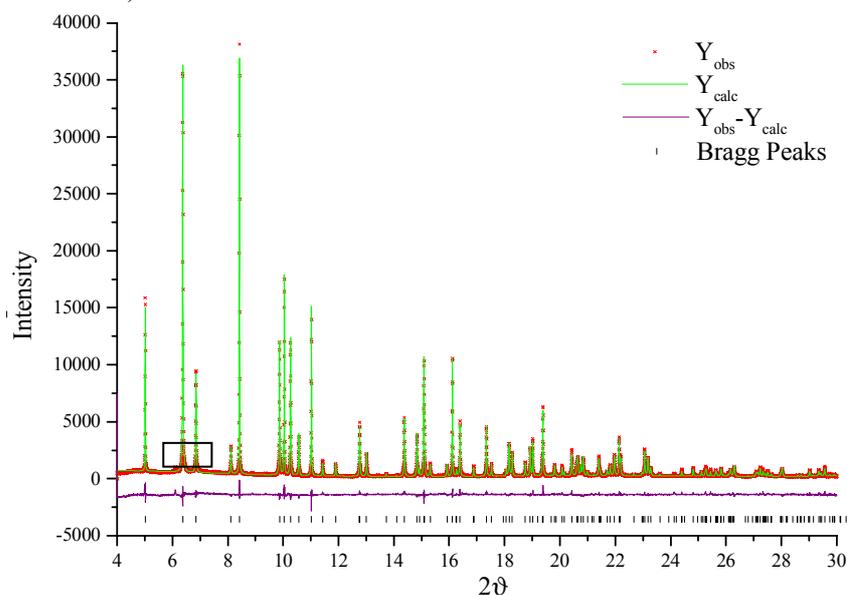

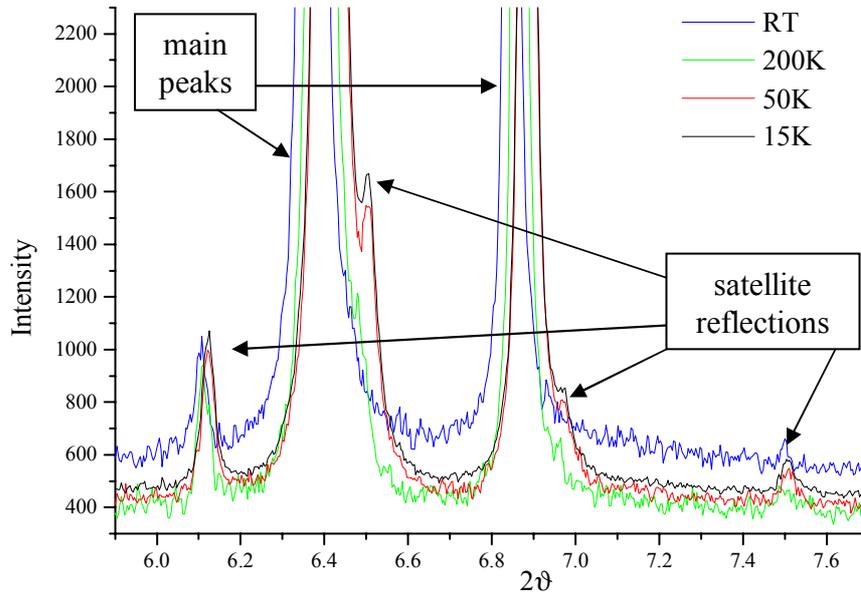**Figure 4 ñ Refined room temperature x-ray data from BM1B, ESRF for Li$_{0.50}$V$_2$O$_5$: intensity as a function of 2ϑ.**

Figure 5 ñ Raw diffraction data, intensity as a function of 2ϑ, showing increasing intensity of satellite peaks in Li$_{0.50}$V$_2$O$_5$ as temperature is decreased from room temperature (blue), through 200K (green) and 50K (red) to 15K (black).

These additional peaks, although thought to be due to ordering of vanadium ions in the crystal structure, were not reflections from a commensurate supercell, but from incommensurately modulated ordering of vanadium ions, defined by a modulation vector, which is dependent on composition and temperature:

$$\mathbf{q}^T = x\mathbf{a}^* + y\mathbf{b}^* + z\mathbf{c}^*$$

With this modulation vector, all the reflections may be indexed by four integers (h, k, l, m) according to:

$$\mathbf{S} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}^{rt}$$

This is consistent with magnetic data collected using a SQUID MPMS-7 and muon spin relaxation experiments, which were indicative of antiferromagnetic correlations but no long range magnetic order in the series.

The compositions for which satellite peaks are observed at room temperature all belong to the ε-phase, where there is a medium lithium content. There is no phase transition in this compositional range to minimise distortion of the vanadium oxide layers; therefore from the results of our high resolution x-ray diffraction experiments at ESRF, we can speculate that charge ordering occurs in this phase to reduce intralayer strain through an as yet undetermined mechanism.

1.   M. Hase, K. Uchinokura, and I. Terasaki, *Phys. Rev. Lett.,* **70,** 3651 (1993).
2.   K. Ishida, Y. Kitaoka, K. Asayama, M. Azuma, Z. Hiroi, and M. Takano, *J. Phys. Soc. Jpn.,* **63,** 3222 (1994).
3.   S. Taniguchi, T. Nishikawa, Y. Yasui, Y. Kobayashi, M. Sato, T. Nishioka, M. Kontani, and K. Sato, *J. Phys. Soc. Jpn.,* **64,** 2758 (1995).
4.   M. Onoda and N. Nishiguchi, *J. Solid State Chem.,* **127,** 359-362 (1996).
5.   M. Onoda and H. Nagasawa, *Phys. Status Solidi B,* **141,** 507 (1987).