

## X-ray anomalous scattering investigations on the charge order in $\alpha'$ - $\text{NaV}_2\text{O}_5$

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Anomalous x-ray-diffraction studies show that the charge ordering in  $\alpha'$ - $\text{NaV}_2\text{O}_5$  is of zigzag type in all vanadium ladders. We have found that there are two models of the stacking of layers along the  $c$  direction, each consisting of two degenerated patterns, and that the experimental data are well reproduced if the two patterns appear simultaneously. We believe that the low-temperature structure contains stacking faults separating regions corresponding to the four possible patterns.

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In recent years  $\alpha'$ - $\text{NaV}_2\text{O}_5$  has raised a great deal of interest as being the second inorganic compound, after  $\text{CuGeO}_3$ , where a quantum antiferromagnetic state is achieved at the expense of a lattice distortion.<sup>1</sup> At  $T_C = 34$  K, it exhibits a structural<sup>2</sup> as well as a magnetic phase transition that lifts the magnetic degeneracy, opening an energy gap ( $\Delta = 9.8$  meV) between the ground state, a non-magnetic spin singlet, and the lowest magnetic spin triplet.<sup>3</sup> NMR experiments<sup>4</sup> have reported one V site above  $T_C$  ( $\text{V}^{4.5+}$ ) but two inequivalent sets of V sites below  $T_C$ , indicating a charge disproportionation of  $\text{V}^{4+}$  ( $3d^1$ ,  $S = \frac{1}{2}$ ),  $\text{V}^{5+}$  ( $3d^0$ ,  $S = 0$ ). These observations suggest that a charge ordering (CO) is actually related to the magnetic ordering of  $\text{V}^{4+}$ - $\text{V}^{4+}$  dimers as well as to the lattice distortion, characterized by the wave vector  $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$ . Therefore,  $\alpha'$ - $\text{NaV}_2\text{O}_5$  cannot be considered as a conventional spin-Peierls compound. To date, the mechanism of the spin-gap formation and the nature of the CO phase transition are not understood, and much effort has been provided to the determination of the magnetic ordering, the crystallographic structure, and the charge ordering.

It is now well accepted that the high-temperature structure space group is  $Pm\bar{m}n$ .<sup>5</sup> It describes a centrosymmetric crystal structure of lattice parameters  $a = 11.325$  Å,  $b = 3.611$  Å, and  $c = 4.806$  Å, where the only V site in the unit cell has a mixed-valence state or a static average charge state  $\text{V}^{4.5+}$ . Below 34 K, a set of weak diffraction peaks appears at  $(h/2, k/2, l/4)$  Bragg positions with an intensity roughly  $10^3$  times weaker than the Bragg peaks of the  $Pm\bar{m}n$  phase. The refinement of the low-temperature (LT) crystal structure<sup>6</sup> has been greatly hindered by the large size of the supercell,  $2a \times 2b \times 4c$ , including 16 unit cells, and therefore, by the large number of atoms to consider. This problem has been circumvented by using a superspace approach,<sup>6</sup> which allows to place some constraints between specific atomic parameters, and finally the LT reflections can be reasonably refined in  $Fmm2$ , a subgroup of  $Pm\bar{m}n$ .

Later, de Boer and co-workers arrived at an identical conclusion by performing a conventional structure refinement on many measured reflections.<sup>7</sup>

$\alpha'$ - $\text{NaV}_2\text{O}_5$  can be seen as a set of layers of two-leg vanadium ladders running along the  $b$  direction with the rungs along the  $a$  direction. V are located inside oxygen squared-base pyramids whose corners shared with neighboring pyramids. The cations  $\text{Na}^+$  are located between the layers. The LT distortions, as determined by Lüdecke *et al.*,<sup>6</sup> concern the pyramids belonging to half of the ladders, indeed modulated and nonmodulated ladders alternate along the  $a$  direction. The displacement highly concerns the "bridge oxygen," at the center of the rung, that is shifted towards one V of the rung, and alternatively to the other V in the next rungs of the ladder. These latter distortions suggest an alternated localization of the charge on one side of the rung<sup>8</sup> along the modulated ladder, whereas nonmodulated ladders remain  $\text{V}^{4.5+}$ , as in the high-temperature phase.

The above structure determination has been questioned by experimental results issued from a wide variety of techniques. The <sup>51</sup>V NMR study<sup>4</sup> has determined only two valence states; Raman spectroscopy<sup>9</sup> measures a number of Raman modes not consistent with the number of possible modes in the  $Fmm2$  structure. One of the most compelling results is probably <sup>23</sup>Na NMR studies<sup>10,11</sup> reporting eight inequivalent Na sites, again in complete disagreement with x-ray refinement. Neutron inelastic scattering<sup>12</sup> and anomalous x-ray scattering<sup>13</sup> results found a zigzag pattern along all the V ladders, but only a single-layer model was considered in their calculations. It is interesting to note that these two structural methods have converged to a similar solution without using *conventional* crystallography methods, whereas *purely* crystallographic refinements are certainly impeded by the inherent complexity of the CO in  $\alpha'$ - $\text{NaV}_2\text{O}_5$ . In this work we present the full charge disproportionation on all the ladders and the stacking sequence along the  $c$  direction in  $\alpha'$ - $\text{NaV}_2\text{O}_5$  by means of anomalous x-ray diffraction.

Anomalous diffraction is a powerful tool in the investigation of charge ordering since the x-ray resonant scattering

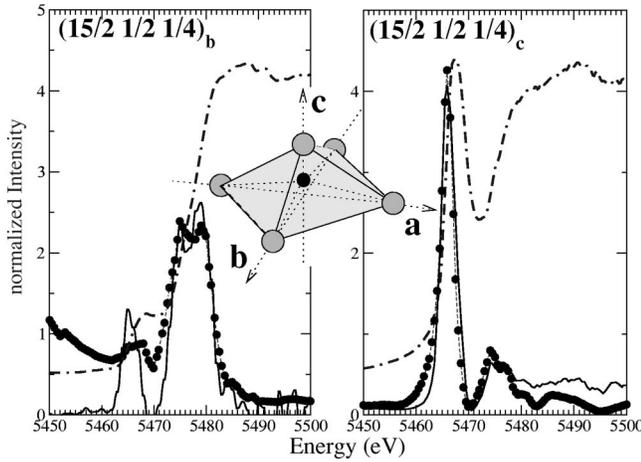


FIG. 1.  $(\frac{15}{2}, \frac{1}{2}, \frac{1}{4})$  reflection (●) and fluorescence spectra (dot-dashed line) taken around the vanadium  $K$  edge with the photon polarization along  $b$  (left panel) and along  $c$  (right panel). The curves have been rescaled for clarity. Left panel: the reflection is compared with  $\partial f''/\partial E$  (solid line). Right panel: the reflection is compared (solid line) with one of the two possible charge ordering models (model 2, Fig. 3). The differences between both polarization states exclusively come from the anisotropy of the vanadium in its pyramidal site (inset).  $a$ ,  $b$ , and  $c$  axes of the pyramid correspond to the direction of the crystallographic axis.

amplitude is specifically related to the density of occupied and unoccupied electronic states at the resonant atom.<sup>14</sup> Besides, the anomalous scattering factor's line shape reflects the charge localization together with the lattice distortion that serves to stabilize the static charge distribution. In  $\alpha'$ - $\text{NaV}_2\text{O}_5$  the observed spin-singlet ordering lead us to assume two defined charge states,  $\text{V}^{4+}$  and  $\text{V}^{5+}$  (no effort has been made to quantify the actual charge transfer yet), distributed in the new supercell according to a certain pattern. As the local atomic configuration remains nearly unchanged by the charge ordering,<sup>6</sup> the resulting anomalous scattering factors (the correction to the Thomson scattering) of both species,  $f^{4+}$  and  $f^{5+}$ , are slightly shifted towards lower ( $\text{V}^{4+}$ ) or higher ( $\text{V}^{5+}$ ) energies with no significant change in the near-edge structure (first 50 eV above the edge). This overall energy shift, amounting a few eV, is known as the *chemical shift*. Mathematically speaking, the above sentence implies that  $f^{5+}(E + \delta E) \approx f^{4+}(E) \approx f^{4.5+}(E + \delta E/2)$ .

The imaginary part of  $f(E)$ ,  $f''(E)$  is proportional to the absorption cross section and typically shows a discontinuity in a steplike form as a function of energy (dot-dashed line in Fig. 1). As a consequence, the chemical shift may reveal dramatic anomalies if the anomalous factors of the two valence states are subtracted, as occurs in x-ray-diffraction experiments for some given, often very weak, reflections. The vanadium anomalous structure factor can be written as  $F \propto c_{4+}f^{4+} + c_{5+}f^{5+} = \frac{1}{2}(c_{4+} + c_{5+})(f^{4+} + f^{5+}) + \frac{1}{2}(c_{4+} - c_{5+})(f^{4+} - f^{5+})$ , where we have dropped the  $Q$  dependence of  $c_{4+(5+)}$  =  $\sum_i^{\text{V}^{4+(5+)}} e^{i\mathbf{Q}\cdot\mathbf{r}_i}$  and the  $E$  dependence of  $f^{4+(5+)}$ . For such specifically chosen reflections one can easily show that  $c_{4+}$  and  $c_{5+}$  are close to being  $\pi$  out of phase and hence  $|c_{4+} + c_{5+}| \ll |c_{4+} - c_{5+}|$ . Indeed,  $c_{4+} + c_{5+} = 0$

if the resonant atoms do not undergo any shift from their original positions in the high-temperature phase. Finally  $F \propto \Delta c \cdot [f^{4+}(E) - f^{5+}(E)] \approx \Delta c \cdot [f^{5+}(E + \delta E) - f^{5+}(E)] \approx \Delta c \cdot (\partial f^{5+}/\partial E) \cdot \delta E$ .<sup>13,15</sup>

Experiments were performed at the ID20 beamline located at the European Synchrotron Radiation Facility (Grenoble, France). An as-grown  $\alpha'$ - $\text{NaV}_2\text{O}_5$  high-quality single crystal was mounted on the cold finger of a closed cycle He refrigerator and data collection was carried out at the base temperature, 13 K. An undulator provided a highly  $\sigma$ -polarized photon flux, and the monochromatization was performed by a Si(111) double crystal with an energy resolution of less than 0.8 eV. Measurement of the polarization components of the diffracted beam was performed by using the (004) reflection of a pyrolytic graphite crystal.

A total of 20 different diffraction peaks of the low-temperature phase have been measured as a function of the incident photon energy and under different photon polarization conditions. The energy step for all the scans was 0.5 eV. In the following we shall use the notation  $(h, k, l)_{b(c)}$  (Ref. 16) to indicate that the  $(h, k, l)$  Bragg intensity has been measured with the incident polarization along the  $b(c)$  direction. We have found that peaks having a strong anomalous contribution are  $(\frac{9}{2}, \frac{1}{2}, \frac{3}{4})_b$ ,  $(\frac{9}{2}, \frac{1}{2}, \frac{5}{4})_b$ ,  $(\frac{11}{2}, \frac{1}{2}, \frac{1}{4})_b$ ,  $(\frac{11}{2}, \frac{1}{2}, \frac{3}{4})_b$ ,  $(\frac{15}{2}, \frac{1}{2}, \frac{1}{4})_b$  and  $(\frac{17}{2}, \frac{1}{2}, \frac{1}{4})_b$ . Energy spectra with the polarization along  $c$  for reflections  $(\frac{15}{2}, \frac{1}{2}, \frac{1}{4})_c$ ,  $(7, 0, \frac{1}{2})_c$ ,  $(7, 1, \frac{1}{2})_c$ ,  $(6, 0, \frac{1}{2})_c$ , and  $(6, 1, \frac{1}{2})_c$  were also measured. Finally high-temperature phase reflections  $(p, 0, 0)_c$  with  $p = 1, 3, 5, 7$  were recorded in both  $\sigma$ - $\sigma$  and  $\sigma$ - $\pi$  geometries.

The  $(\frac{15}{2}, \frac{1}{2}, \frac{1}{4})_c$  peak has a huge anomaly at 5466 eV (see Fig. 1, right panel), as Nakao *et al.*<sup>13</sup> have also found, in contrast with  $(\frac{15}{2}, \frac{1}{2}, \frac{1}{4})_b$ , where this feature has nearly disappeared (Fig. 1, left panel).  $(p, 0, 0)_c$  peaks are extinct in the high-temperature phase because of the  $n$ -glide plane, and therefore one expects an anomalous signal in the  $\sigma$ - $\pi$  channel alone. The lack of anomalous signal in the  $\sigma$ - $\sigma$  channel below  $T_C$  in the  $(p, 0, 0)_c$  and in the  $(h, k, \frac{1}{2})_c$  reflections is a key feature that we shall use below.

Fluorescence spectra with the incident photon polarization along the  $b$  and  $c$  directions were obtained by removing the analyzer crystal and turning the sample off the Bragg reflection by  $1^\circ$  (Fig. 1). The two spectra evidence a strong anisotropy with the polarization direction due to the anisotropy of the V site. They were used to extract  $f''$ , and the real part of the anomalous correction,  $f'$ , is calculated through the Kramers-Kronig transformation of  $f''$ .<sup>14</sup>

The reflection  $(\frac{15}{2}, \frac{1}{2}, \frac{1}{4})$  (in all measured polarizations) is of very special importance since the energy dependence of the scattered intensity clearly suggests a *derivative* effect (Fig. 1), with  $|c_{4+} + c_{5+}| \rightarrow 0$ . The remainder of  $(h/2, k/2, l/4)$  Bragg peaks also manifests an analogous *derivative* effect although hidden by a larger  $|c_{4+} + c_{5+}|$  factor. Charge attribution is performed by inspecting the phase factor  $e^{i\mathbf{Q}\cdot\mathbf{r}_i}$  of each atomic position,  $\mathbf{r}_i$ . An atom located at  $(x, y, z)$  has a phase factor of opposite sign with respect to atoms at  $(x + 1, y, z)$ ,  $(x, y + 1, z)$ ,  $(x, y, z + 2)$ , and  $(x + 1, y$

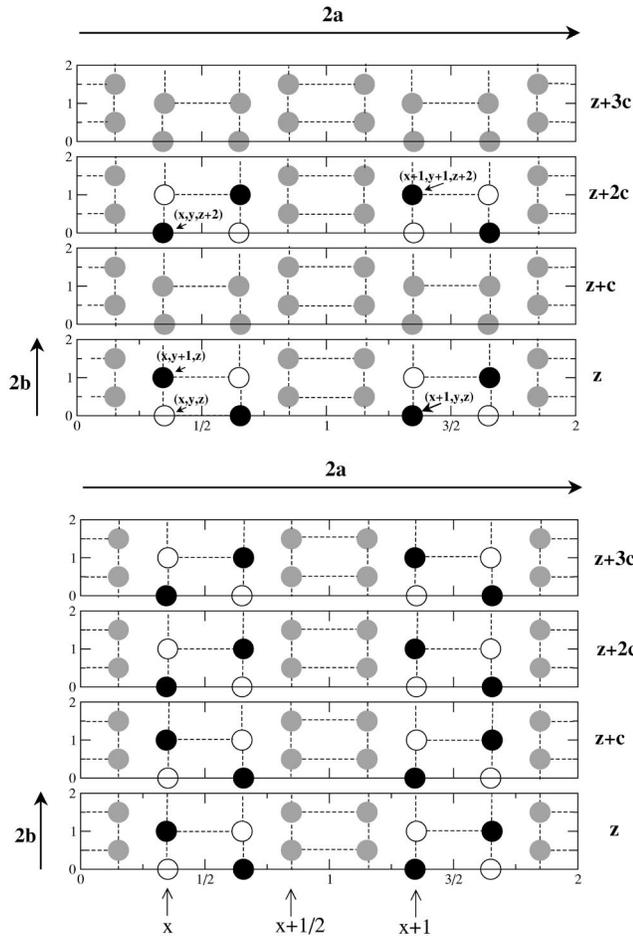


FIG. 2. Schematic representation of vanadium atoms in the three-dimensional structure of  $\alpha'$ - $\text{NaV}_2\text{O}_5$ . Charge attribution is based on the use of the *derivative* concept for the  $(h/2, k/2, l/4)$  reflections (top panel) and of the extinction rule found in reflections such as  $(6, 0, \frac{1}{2})_b$  (bottom panel). Black (open) circles are  $\text{V}^{4+}$  ( $\text{V}^{5+}$ ) and gray circles represent yet unassigned valences.

$+1, z+2$ ), therefore, we assign different charge states to them to initiate the *derivative* effect. Moreover, the charge transfer between rungs should be zero (thus implying a charge disproportionation in the same rung) in order to ensure the insulating state below  $T_C$ . This first step of the valence distribution is shown in Fig. 2 (upper panel). The simple rule found in our spectra readily implies that the V atoms of different valences have to be arranged in zigzag and excludes  $\text{V}^{4+}\text{-V}^{4+}\text{-}\dots$  chains along the  $b$  direction.

For the  $(6, 0, \frac{1}{2})_c$  peak, no anomalous signal has been detected, and therefore all V contributions to the structure factor have to cancel out. Atoms in the same  $(a, b)$  plane have an identical phase factor, whereas atoms located at  $z+1$  have a phase factor of opposite sign. Therefore, we infer that the second layer along the  $c$  direction should exhibit the same CO pattern as the first one, and identically between layers 3 and 4, as is shown in Fig. 2 (lower panel).

Finally, an atom at  $x$  has a phase difference equal to  $\pi$  with respect to atoms at  $x + \frac{1}{4}$  for  $(p, 0, 0)$   $p$  odd peaks. Extinction for these reflections immediately implies that ladders

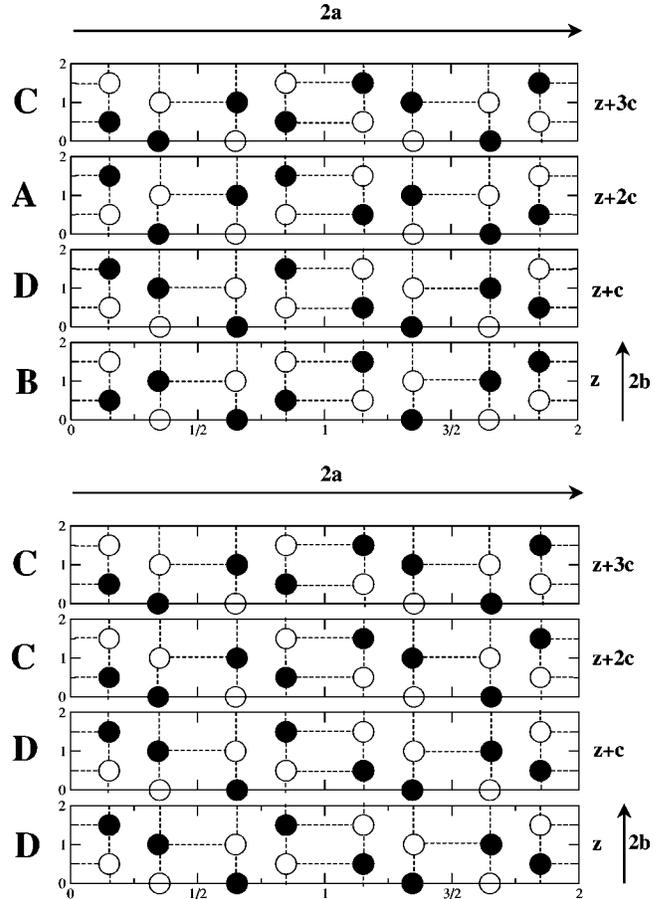


FIG. 3. Possible models of CO resulting from the extinction condition of  $(p, 0, 0)_c$   $p$  odd reflections. Each different layer has been labeled (A, B, . . .) and we will refer to a particular model by writing the stacking sequence. Top panel is model 1, BDAC, where each layer has a different arrangement, and appears coupled to the complementary, DBCA (not shown). Bottom: Model 2, DDCC, which, as in model 1, has to come in with its complementary, BBAA (not shown).

centered at  $x=1$  have to be modulated as those at  $x=\frac{1}{2}$ . By applying the above-mentioned conditions, *derivative* in  $(\frac{15}{2}, \frac{1}{2}, \frac{1}{4})$  and the absence of intensity in the  $(6, 0, \frac{1}{2})_c$  peak, to the ladders at  $x=1$ , one gets the patterns in Fig. 3. V-extinction considerations in the above set of Bragg reflections yield CO in all ladders and therefore rule out the  $Fmm2$  space group. Note that no fit has been needed so far.

At this stage of our deductions, we are confronted with four models originating from the four different ways that the zigzag pattern on one ladder can be shifted along the  $b$  direction with respect to the neighboring one (Fig. 3). Only ladders centered at  $x=0$  and at  $x=1$  (and equally the ladders at  $x=\frac{1}{2}$  and  $x=\frac{3}{2}$ ) are related to ensure the *derivative* effect. In order to proceed further we have performed a detailed analysis of the line shape of different superlattice reflections with all four possible models.

Diffraction intensities as a function of energy have been calculated from the structure factor of the LT unit cell using standard tabulated scattering factors (nonresonant) and anomalous scattering factors of the V atoms for the two po-

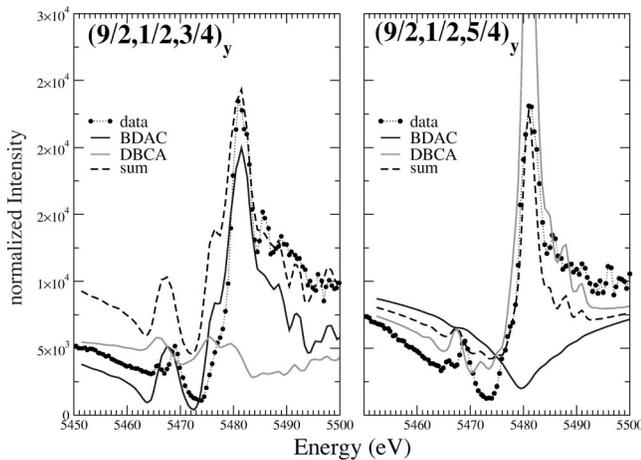


FIG. 4. Diffracted intensity versus photon energy data of peaks  $(\frac{9}{2}, \frac{1}{2}, l/4)_y$ , with  $l=3$  (left) and  $l=5$  (right) and results of simulations with model 1. Simulations with model 2 yield identical quality results. Whereas the pattern BDAC reproduces well the  $l=3$  peak, it is the DBCA pattern that better reproduces the line shape for the  $l=5$  peak. The best result for both reflections is achieved when both degenerate patterns are summed (dashed line).

larization directions. Appropriate anomalous scattering factors for  $V^{4+}$  and  $V^{5+}$  have been obtained by shifting [of  $\delta E = \pm 0.9$  eV (Ref. 13)]  $f'$  and  $f''$  obtained as described above. The simulation of reflections  $(\frac{9}{2}, \frac{1}{2}, \frac{3}{4})_b$  and  $(\frac{9}{2}, \frac{1}{2}, \frac{5}{4})_b$  shows that none of the BDAC or DBCA patterns of model 1 alone can reproduce both reflections, as is shown in Fig. 4.

The same occurs for the DDCC and BBAA patterns of model 2 (not shown). In order to obtain better values of the phases, V-atom displacements along  $a$  and  $c$  have been introduced in the fit, consistently with the charge modulation. Indeed the sum of patterns BDAC and (the complementary) DBCA of model 1 and, equally, the sum of patterns DDCC and AABB of model 2 perfectly account for the energy dependence of all measured reflections. In order to accommodate these findings, the actual low-temperature structure of  $\alpha'$ - $\text{NaV}_2\text{O}_5$  should contain either domains, related to the stabilization of a monoclinic structure, or stacking faults of model 1 or model 2 or of both together. The first solution implies the presence of split Bragg reflections, which have been observed neither in our experiments nor in van Smaalen's work.<sup>17</sup> The second solution implies a degenerated ground state which should give rise to very complicated phase diagrams. The x-ray-diffraction results under pressure (and temperature) by Ohwada *et al.*<sup>18</sup> nicely show the development of a series of modulation wave vectors along the  $c^*$  direction. This sequence, qualitatively understood within the framework of devil's-staircase-type phase transitions, reflects the presence of competing arrangements along  $c$  of nearly degenerate units, as those proposed in this paper.

To conclude, our x-ray anomalous diffraction data have allowed to solve a very controversial and standing problem, the charge ordering pattern in  $\alpha'$ - $\text{NaV}_2\text{O}_5$ . We have found that all vanadium ladders are modulated, and different stacking sequences along the  $c$  direction coexist in the structure.

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