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# Anomalous structural behaviour of Zn-doped $\text{LiV}_2\text{O}_4$

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## 1. Introduction

The cubic spinel compound  $\text{LiV}_2\text{O}_4$  has been discussed as the first example of a heavy fermion compound without f-electrons [1]. Based on a wealth of experimental observations, a phenomenological heavy-fermion-like behaviour at low temperatures is now well established [2]. This low-temperature state is characterized by the evolution of antiferromagnetic (afm) spin correlations, whereas ferromagnetic (fm) spin correlations dominate at elevated temperatures [3]. In particular,  $\text{LiV}_2\text{O}_4$  revealed an anomalous temperature dependence of the lattice constants and thermal expansion [4,5]. A strong decrease of the unit cell

volume below  $T=20$  K is indicative of a strong electron–phonon coupling that can be described in terms of an enhanced electronic Grüneisen parameter, which again is a characteristic property of heavy fermion systems. On the other hand, a strong coupling between electronic and lattice degrees of freedom is a frequently encountered property of transition-metal oxides. Alternative explanations for the unusual physical properties of  $\text{LiV}_2\text{O}_4$  have been proposed in terms of strongly enhanced spin fluctuations due to the frustration of the spinel structure for nearest neighbour afm interactions [6]. A strong magneto-elastic coupling has been found and the ground state may change from fm to afm, depending on the exact oxygen position [6]. The important role of frustration is also evidenced by doping experiments. For  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  the introduced atomic disorder rapidly results in a spin-glass state over a wide concentration range [7]. In order to obtain more

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insight into the relationship between the crystal structure and electronic properties, high-resolution neutron powder diffraction experiments on  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  have been performed.

## 2. Experimental results and discussion

Polycrystalline samples of  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  ( $x=0.05$  and  $0.2$ ) have been synthesized as described elsewhere [8]. The neutron powder diffraction experiments have been performed on the high-resolution diffractometer HRPT [9] installed at the Swiss spallation neutron source SINQ of the PSI Villigen, Switzerland. In the present case, the Ge (5 3 3) reflection corresponding to an incident neutron wavelength of  $1.494 \text{ \AA}$  has been employed. Diffraction patterns were recorded with an angular step width of  $0.05^\circ$ . Carefully powdered samples were filled in a vanadium container and mounted in a cryostat allowing for temperatures  $1.5 \text{ K} < T < 300 \text{ K}$ . The raw data were corrected for detector efficiency by a vanadium standard. The resulting diffraction pattern were analyzed by standard Rietveld refinement employing the FULLPROF [10] program. The data could be well fitted within the nominal FCC spinel structure for which a statistical distribution of Li and Zn was assumed. Within the Rietveld refinement, the following parameters have been fitted: cubic lattice constant, oxygen positional parameter, four resolution parameters, two asymmetry parameters, Li/Zn occupancy, zero point shift, overall isotropic temperature factor and six polynomial background parameters. Additionally, very small peaks at angular positions around  $40^\circ$ ,  $117^\circ$  and  $150^\circ$  show up due to a spurious phase. A systematic search of possible parasitic phases revealed that these peaks are most probably due to some small residuals of the starting material  $\text{LiVO}_3$ . Including this second phase into the fit resulted in excellent agreement between measured and calculated intensities of  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  with reliability factors of 0.04 (or slightly below) for all temperatures investigated. Table 1 summarizes the crystallographic properties of  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  at  $T=1.5 \text{ K}$ . Fig. 1 shows the temperature dependence of the

Table 1

Crystallographic properties of  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  ( $x=0.05, 0.2$ ) at  $T=1.5 \text{ K}$  resulting from the Rietveld refinements

| $T=1.5 \text{ K}$  | $x=0.05$           | $x=0.2$            |
|--------------------|--------------------|--------------------|
| $a \text{ (\AA)}$  | 8.23835(10)        | 8.28030(10)        |
| $x \text{ (O)}$    | 0.2610(3)          | 0.2605(8)          |
| Occ./Conc. (%) Zn  | 0.0028(8)/6.71(19) | 0.0110(8)/26.4(10) |
| $B_{\text{ov}}$    | 0.344(12)          | 0.381(12)          |
| Asy1               | 0.199(9)           | 0.214(8)           |
| Asy2               | 0.0334(3)          | 0.032(3)           |
| $R_{\text{Bragg}}$ | 0.039              | 0.039              |

Listed are the cubic lattice constant  $a$ , the oxygen positional parameter  $x$ , Zn occupancy/concentration, the isotropic temperature factor  $B_{\text{ov}}$ , the two asymmetry parameters Asy1 and Asy2, and the residual  $R_{\text{Bragg}}$ .

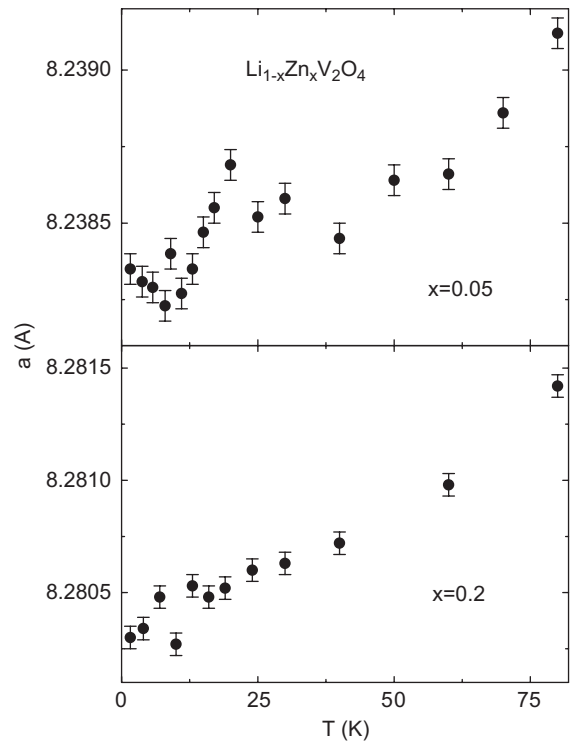


Fig. 1. Temperature dependence of the lattice constant of  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ , as determined by the Rietveld refinements.

lattice parameter  $a$  of  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  for  $x=0.05$  (upper frame) and  $x=0.2$  (lower frame). As evident from Fig. 1,  $\text{Li}_{0.95}\text{Zn}_{0.05}\text{V}_2\text{O}_4$  exhibits a significant and well defined anomaly of  $a(T)$  around  $T=20 \text{ K}$ , similar to what has been

observed for pure  $\text{LiV}_2\text{O}_4$  [4]. For 20% Zn doping, this anomaly is strongly suppressed. In pure  $\text{LiV}_2\text{O}_4$  an anomalous temperature dependence of the lattice constant has been used to derive an enhanced electronic Grüneisen parameter  $\Gamma_e \approx 25$  [4]. An order-of-magnitude estimate of the electronic Grüneisen parameter is also possible for the present Zn-doped compounds. Recalling the relation  $\Gamma_e(T) = V_m \beta(T) / \kappa C_e(T)$  with  $V_m$  being the molar volume,  $\kappa$  the compressibility,  $\beta$  the volume thermal expansion coefficient and  $C_e$  the electronic part of the specific heat [11], the following values can be inferred on the basis of the present neutron powder diffraction study: For  $x = 0.05$ ,  $\alpha(T = 7 \text{ K}) = 8.2382 \text{ \AA}$  corresponding to a molar volume of  $V_m = 3.367 \times 10^{-4} \text{ m}^3/\text{mol}$ . For  $x = 0.2$  a molar volume of  $V_m = 3.419 \times 10^{-4} \text{ m}^3/\text{mol}$  is obtained. Taking the measured lattice constants in the low-temperature region results in  $\beta(x = 0.05) = 1.4 \times 10^{-5} \text{ K}^{-1}$  and  $\beta(x = 0.2) = 4.5 \times 10^{-6} \text{ K}^{-1}$ . For the compressibility, a value of  $\kappa \approx 5 \times 10^{-10} \text{ m}^2/\text{N}$  is employed, as found in many similar transition-metal oxides including the spinel prototype  $\text{MgAl}_2\text{O}_4$ . Recent measurements on doped  $\text{LiV}_2\text{O}_4$  gave approximate values for  $C_e$  (around 10 K,  $C_e \approx 1.5 \text{ J/mol K}$ ) [12]. Taking these values results again in a strongly enhanced Grüneisen parameter at low temperatures:  $\Gamma_e(x = 0.05, T = 7 \text{ K}) \approx 60$  and  $\Gamma_e(x = 0.2, T = 5 \text{ K}) \approx 20$ . This rather qualitative analysis confirms an intimate relationship between the electronic properties and the crystal lattice of pure and Zn-doped  $\text{LiV}_2\text{O}_4$ . Importantly, the overall crystal structure, in particular the symmetry of the crystal lattice is preserved down to lowest temperatures.

Employing a purely ionic picture (which is of course a strong simplification), the interatomic distances may be compared to the sum of the Shannon ionic radii [13]. It is found that the interatomic distances are smaller than the sum of the ionic radii of the metal ions and oxygen, assuming a fourfold oxygen coordination as

expected for the spinel structure. On the other hand, a good agreement is observed supposing threefold coordinated oxygen ions. Since oxygen has three nearest-neighbour vanadium and one Li ion within the spinel structure of  $\text{LiV}_2\text{O}_4$ , this result seems to reflect strong hybridization effects between oxygen and vanadium. The subtle structural changes may also indicate that orbital degrees of freedom are involved in the evolution of the low temperature heavy-fermion-like behaviour of  $\text{LiV}_2\text{O}_4$ . The present structural data may serve as a new basis for refined electronic structure calculations [2,6].

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