Poster

Incommensurate structures and radiation damage in K2V3O8 and Rb2V3O8 mixed-valence vanadate fresnoites

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Structures of K2V3O8 and Rb2V3O8 mixed-valence vanadate fresnoites are studied with synchrotron single-crystal diffraction at the Swiss Norwegian Beamlines at the ESRF at low temperatures and ambient pressure. K2V3O8 exhibits a phase transition to an incommensurately modulated structure at about 115 K. At 100 K, the satellite reflections can be indexed with two q vectors: q1 = (α,α,0.5) and q2 (-α,α,0.5), where α ≈ 0.3. Although no mixed satellite reflection are observed, the modulated structure is better described in (3+2) than in (3+1) dimensional space - superspace groups P4bm(αα½)(-αα½)0gg and Cmm2(0β½)s00, respectively. The latter includes two twin domains originating from the loss of the 4-fold axis. The geometries of the VO4 and VO5 building units in both models are rigid and it is mainly slight rotations of these polyhedra and small variation of the inter-mediate K-O distances that are modulated [2].

As a large number of single crystal measurements was performed in the temperature range 88–298 K, the newly developed option of cyclic refinements for single crystal data, which was recently incorporated into Jana2020 [3], was used.

The prolonged exposure to the high-brilliance synchrotron beam suppresses the incommensurate phase. The previously postulated phase transition to the incommensurate phase in Rb2V3O8 at 270 K [1] is not observed in our data. One of the reasons could be that the intense radiation also affects the modulation in this material. Our results imply that the detection of weak satellites in incommensurate phases is difficult as the prolonged exposure to a high-brilliance synchrotron beam could lead to the disappearance of subtle modulations. Strategies to collect and analyze single-crystal diffraction data measured with very intense synchrotron radiation using modern low-noise pixel area detectors are discussed.

[1] Withers, R., Höche, T., Liu, Y., Esmaeilzadeh, S., Keding, R. & Sales, B. C. (2004). J. Solid State Chem. 177, 3316.

[2] A. Grzechnik, V. Petricek, D. Chernyshov, C. McMonagle, T. Geise, H. Shahed, K. Friese (2023), Acta Crystallogr. B79, 104.

[3] Petricek, V., Dusek, M. & Palatinus, L. (2014), Z. Kristallogr. 229, 345.