Phase transitions and thermal expansion of polymorphic CoMoO_4

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$CoMoO_4$ exists in three different polymorphs: the standard modification α-$CoMoO_4$ [1], a high-temperature phase β-$CoMoO_4$ which is isostructural to α-$MnMoO_4$ [2] and a high-pressure form $CoMoO_4$-II with wolframite-type structure [3]. All phases remain metastable at ambient condition, $CoMoO_4$-II if pressure is released after cooling to room temperature, β-$CoMoO_4$ after moderate cooling not below room temperature and avoiding mechanical stress. α- and β-phases are isosymmetric polymorphs, and the $\alpha \rightarrow \beta$ transition was ovserved in a DSC experiment at 703 K during heating at a rate of 2 K/min. The high-pressure form $CoMoO_4$-II transforms irreversibely into the β-phase at 856.4 K for a heating rate of 10 K/min with a transition enthalpy of -46.8 J/g. Phase transitions and thermal expansion behaviour was investigated by powder diffraction at beamline B2 [4]. The relative changes of lattice parameters with temperature, normalized to the 300 K values, are shown in Fig. 1.

The principal-axes systems of the thermal expansion tensors can rotate about the monoclinic axes. We have applied the approach of calculating the thermal expansion coefficients in differential limit as outlined in [5]. In a first step polynomial fits up to third order in temperature are determined for the temperature dependence of lattice parameters as shown in Fig. 1 as drawn lines. The coefficients of the second-rank tensors are calculated according to general eq. (13) in [5], which can be simplified for the monoclinic case to previously reported expressions [6]. Eigenvalues and eigenvectors are determined for selected temperatures and shown in Fig. 2. Note that the principal values ξ_2 and ξ_3 can cross each other without ambiguity concerning the principal-axes system because of the restrictions by monoclinic symmetry. The angles φ_ξ of $\vec{\xi_1}$ against the a-axis of the principle-axes systems for the three monoclinic $CoMoO_4$ phases and in comparison to isostructural α- and β-$NiMoO_4$ are shown in Fig. 3. $\vec{\xi_2}$ points along the b-axis, and $\vec{\xi_3}$ completes a right-handed orthonormal system.

The rotations about the monoclinic axes with temperature are much larger for the Co-compounds than for the similar Ni-molybdates. The principle-axes systems are nearly fixed for the α-phases with respect to the crystal axes. This is rather surprising, because the most pronounced anisotropy in thermal expansion is also observed for the α-phases, including even a negative principle value $\xi_{1,\alpha}$.

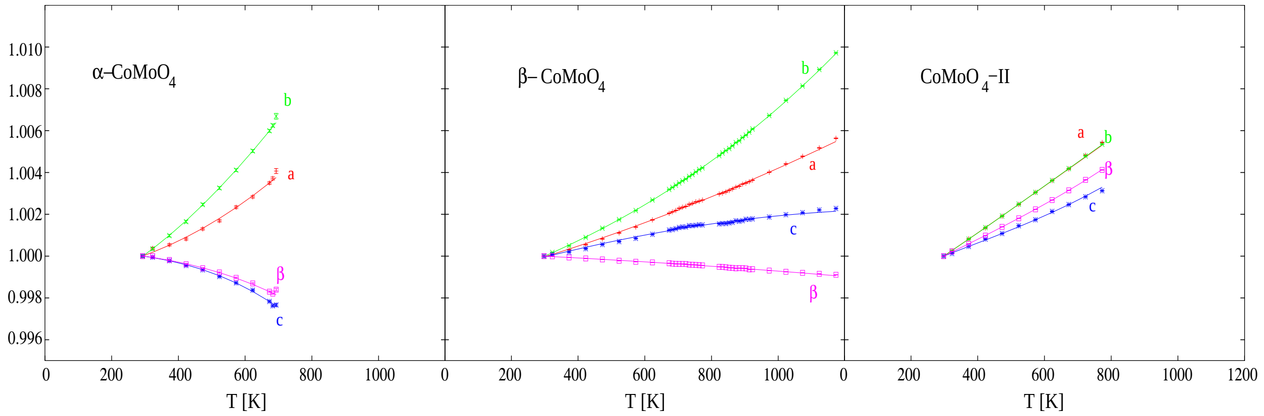

Figure 1: Thermal expansions of all $CoMoO_4$ phases.

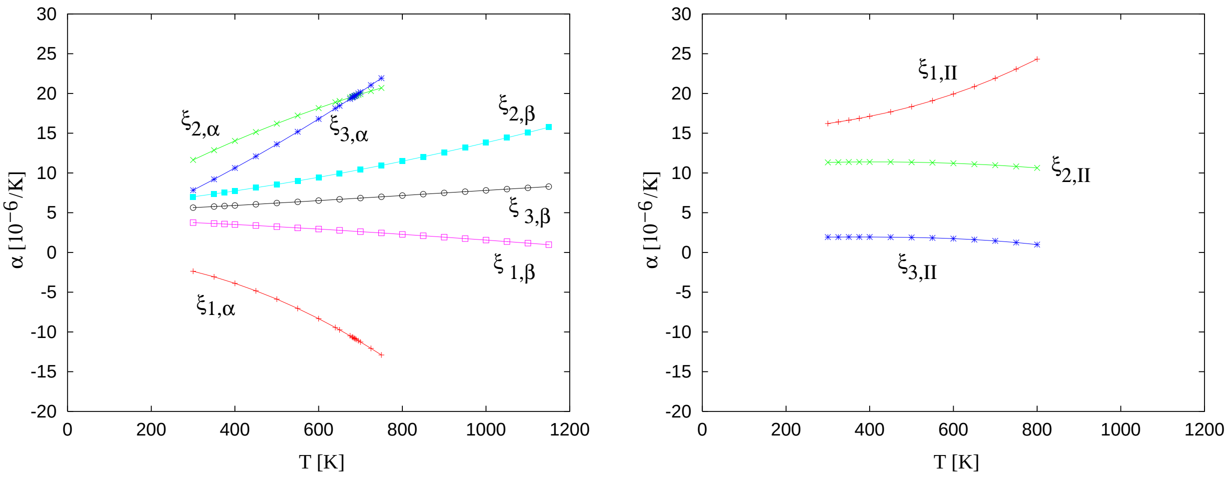

Figure 2: Principal values of the linear thermal expansion tensors for α- and β-CoMoO$_4$ on the left, for CoMoO$_4$-II on the right.

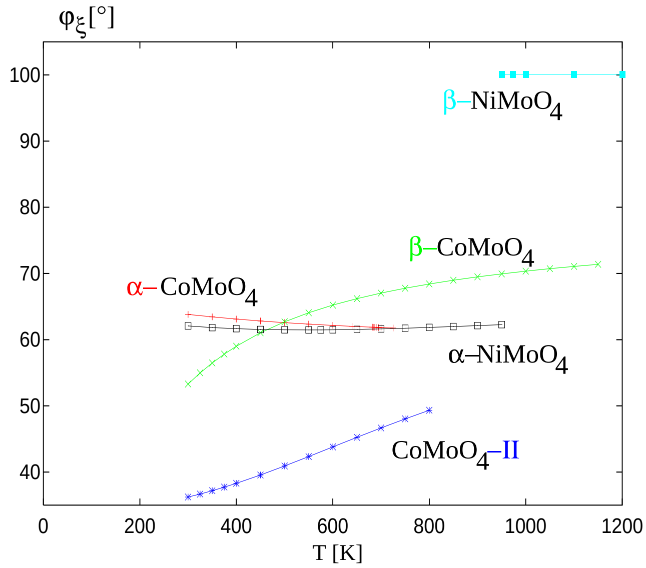

Figure 3: Rotations of the principal-axes systems about the monoclinic axes with temperature.

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