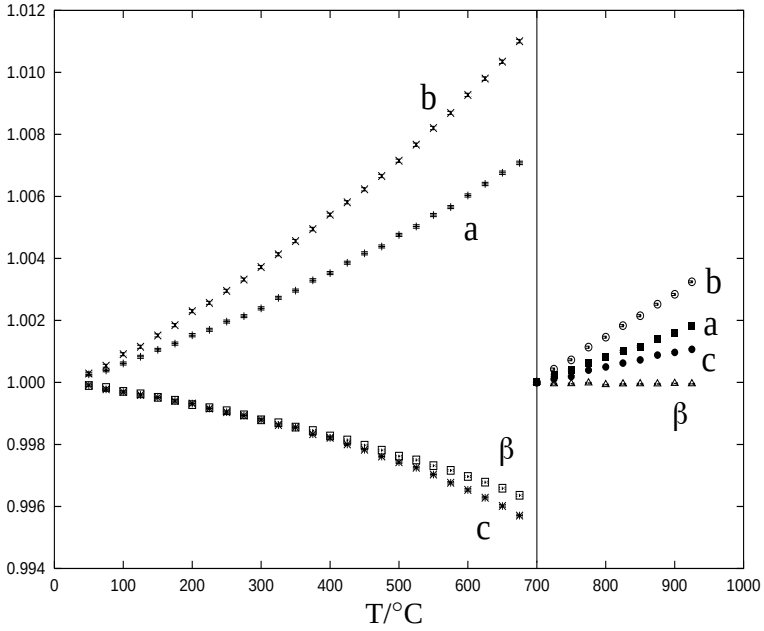
$\alpha \rightarrow \beta$-$NiMoO_4$ transition at high temperature

H. Ehrenberg, M. Knapp, H. Weitzel

Institute for Materials Science, Darmstadt University of Technology
Petersenstr. 23, D-64287 Darmstadt

α-$NiMoO_4$ [1] transforms into the high-temperature modification β-$NiMoO_4$ at about 700°C. This phase transition is reconstructive and results in a different coordination for the molybdenum ions: All Mo-ions are octahedrally coordinated in the α-phase, but tetrahedrally in β-$NiMoO_4$. Based on the structure model of β-(Fe,Co)MoO_4 [2], obtained from an X-ray single crystal structure analysis, the structure of β-$NiMoO_4$ between 700°C and 925°C was refined by the Rietveld method using the software package WINPLOTR. Powder diffraction data were collected in steps of 25°C at beamline B2, using the STOE capillary furnace and the on-site readable image-plate detector OBI [3]. A representative pattern, i. e. intensity versus diffraction angle 2Θ (in °), for the β-phase at 725°C is shown together with calculated profiles and difference curve on the next page. The selected wavelength was λ = 0.69962(1) Å. Impurities between 0.5-1 weight-% NiO and between 2.5 and 3 weight % MoO_2 have been taken into account. α- and β-phases are isosymmetric in space group $C2/m$ with the following unit cell parameters: a = 9.5670(5) Å, b = 8.7391(4) Å, c = 7.6502(3) and β = 114.243(3)° for α-$NiMoO_4$ at 25°C and a = 10.1588(4) Å, b = 9.2135(4) Å, c = 7.0034(2) Åand β = 107.099(2)° for β-$NiMoO_4$ at 700°C, respectively. The estimated standard deviations are calculated in agreement with [4]. The $\alpha \rightarrow \beta$ phase transition is accompanied by a discontinuous increase in the unic cell volume of 5.5%. The largest thermal expansion is along the b-axes for both phases, but the monoclinic angle is decreasing with temperature for the α-phase in contrast to a nearly constant value for the high-temperature structure, see figure below.



The lattice parameters of α-and β-$NiMoO_4$ are normalized to their values at 25°C and 700°C, respectively, as given above.The rather fast data collection rate of about 10 minutes per temperature point (for reaching equilibrium and measuring a full diffraction pattern) allows for very reliable investigations of subtle structural details of phase transitions and chemical reactions.

References

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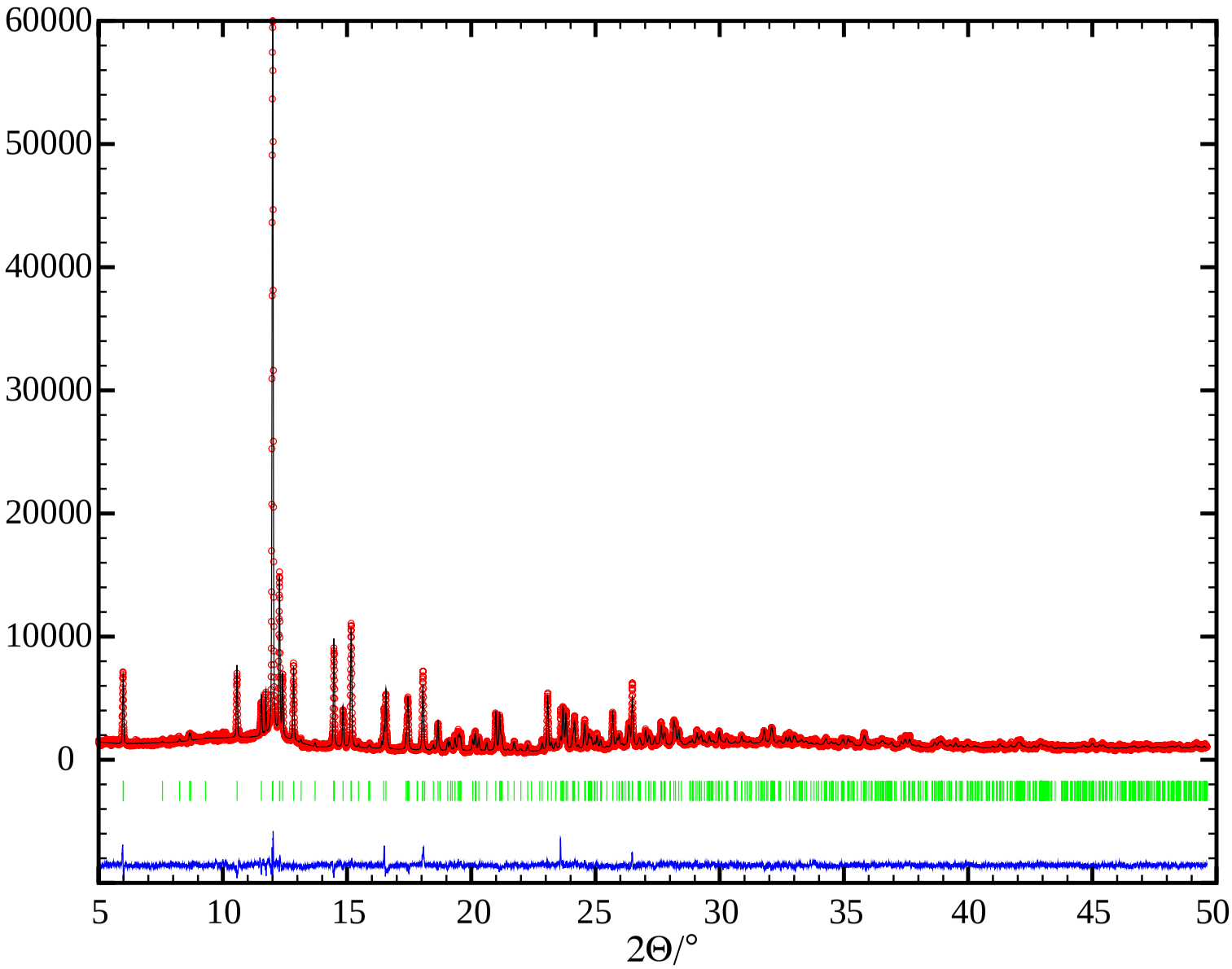
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