*Supplementary Material for*

# [Ni(MeCN)($H_2O$)$_2$($NO_3$)$_2$] (15-crown-5) MeCN: Detailed Study of a Four-Phase Sequence


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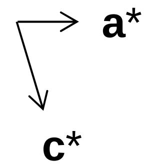
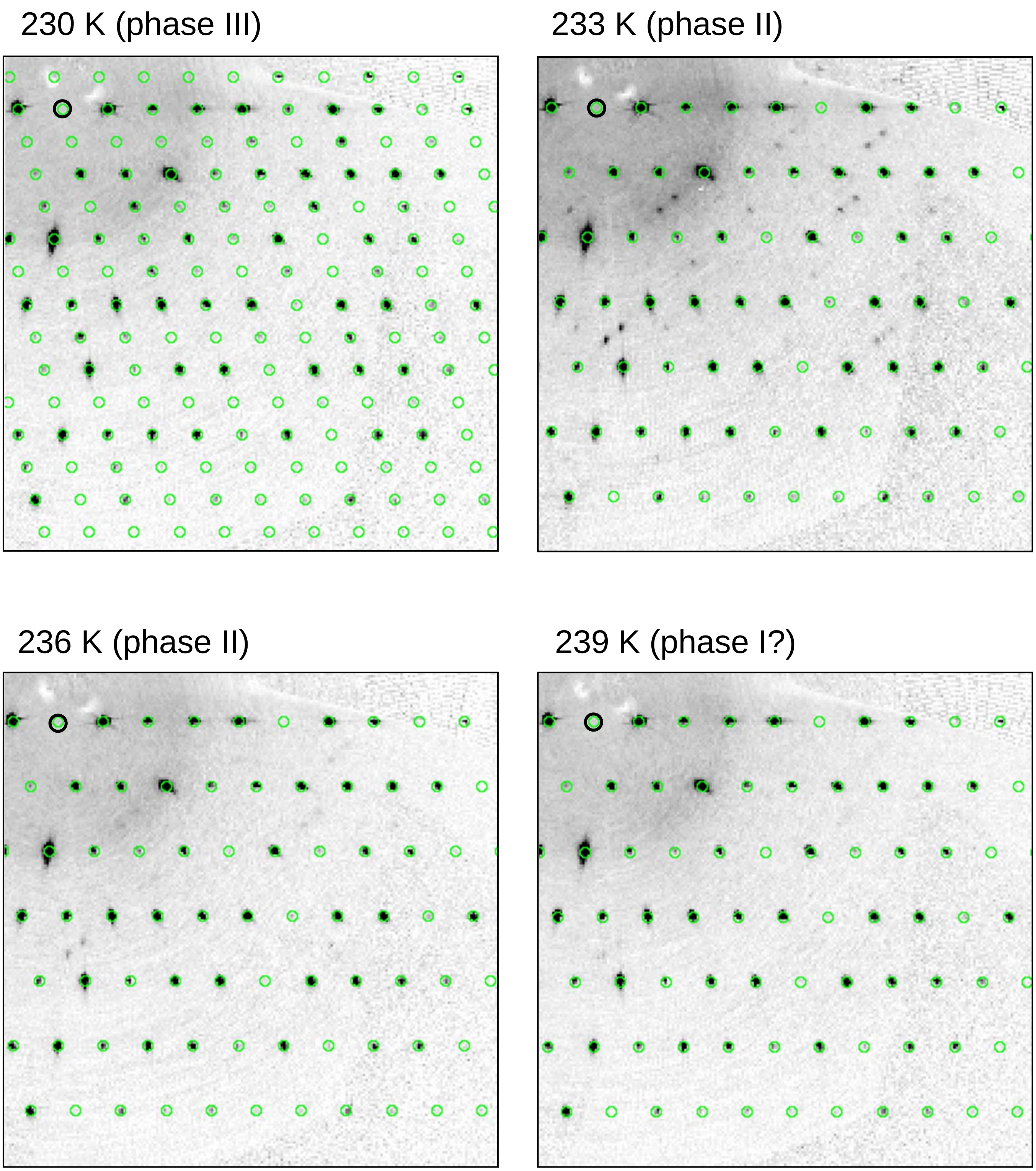
**Synopsis**: The structure of single-crystal acetonitrilediaqua-$\kappa^1$*O*-nitrato-$\kappa^2$*O*-nitratonickel(II) 15-crown-5 acetonitrile solvate was studied at intervals of *ca*. 10 K in the range 90 – 273 K as the crystal passed, without obvious damage, through three phase transitions. The phase sequence, which includes an intermediate, modulated phase, is very similar to that found for [Ni($H_2O$)$_6$]($NO_3$)$_2$·(15-crown-5)·2$H_2O$.


1. Parts of *h*1*l* reciprocal-lattice slices at 230, 233, 236, and 239 K showing the diffraction pattern during the transition into and out of phase II (1 pg.)
2. Parts of *h*0*l* reciprocal-lattice slices in the range 90 – 140 K (10 K intervals) showing the decrease in intensity of the *h*0*l*, *l* odd reflections with the approach of the transition from phase III to phase IV (1 pg.)
3. Reciprocal-lattice slices for the $B2_1$ phase at 90 K and phase II at 233 K that show the two structures are probably the same (8 pp.)
4. Reciprocal-lattice slices *nkl*, *n* = 0 – 3 for the $P2_1$ cell at 90 K that show that there is no **b*** component to the streaks (4 pp.)
4. Ellipsoid plot for the $B2_1$ structure (assumed to be phase II) at 90 K (1 pg.)
5. Detailed description of the disorder in the $B2_1$ structure (assumed to be phase II) at 90 K (3 pp.)
6. Cell dimensions determined for the basic cell ($P2_1/m$, $Z'$ = ½) of phase II within its range of stability (1 pg.)

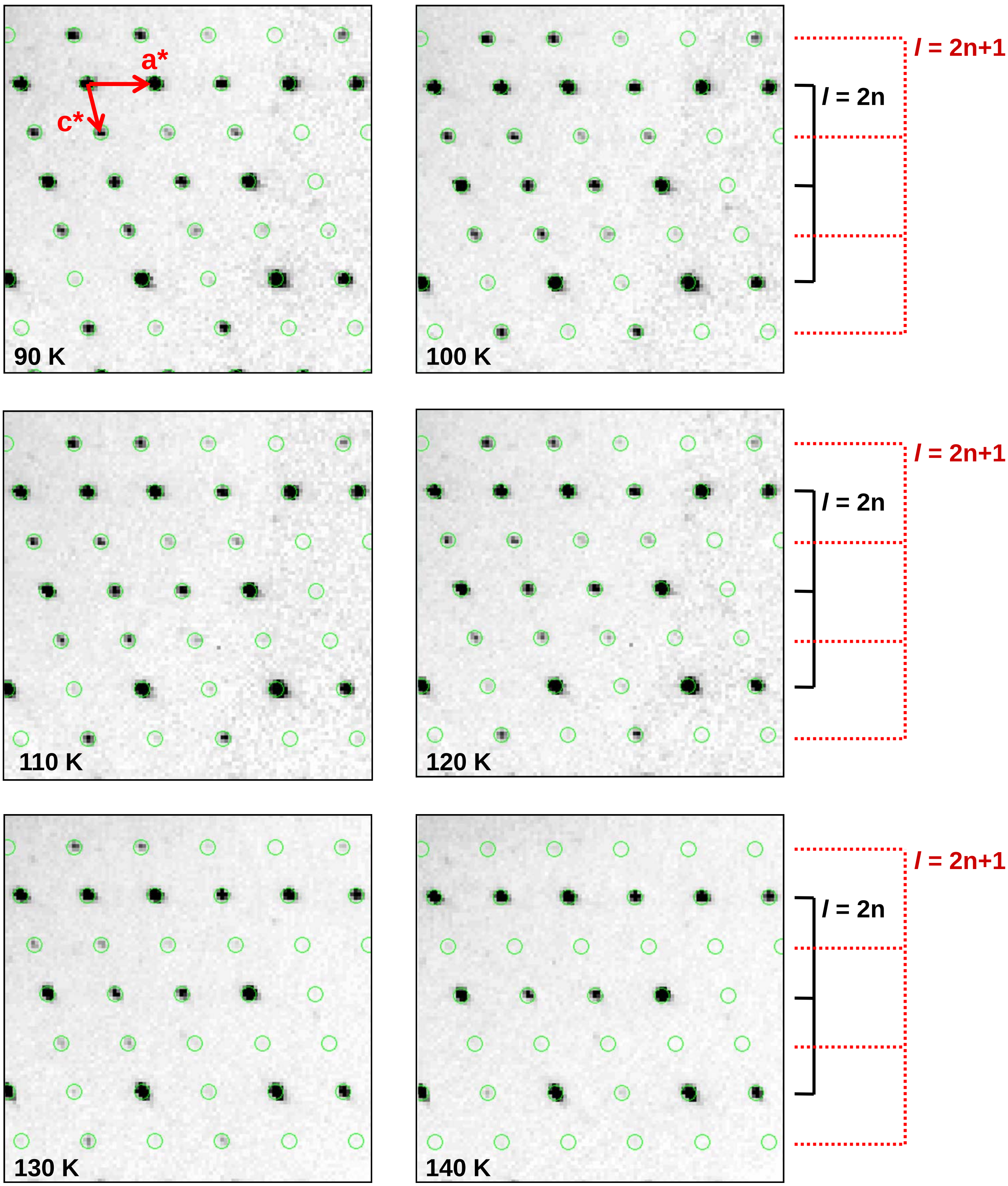
*h*1*l* reciprocal-lattice slices at four temperatures within and near the stability range of phase II (indexing in the $P2_1/m$ phase I cell = basic cell )




(The green circles mark calculated positions of reflections)

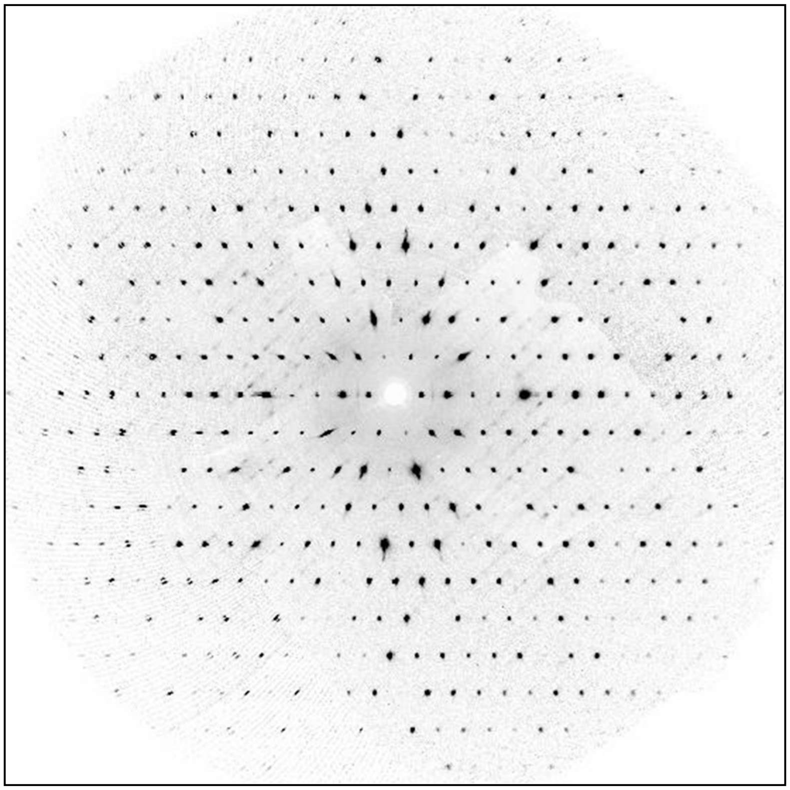
Parts of *h0l* reciprocal-lattice slices as the transition IV→III is approached from below
(axial system originates at reflection 4 0 2)




(The green circles mark calculated positions of reflections)

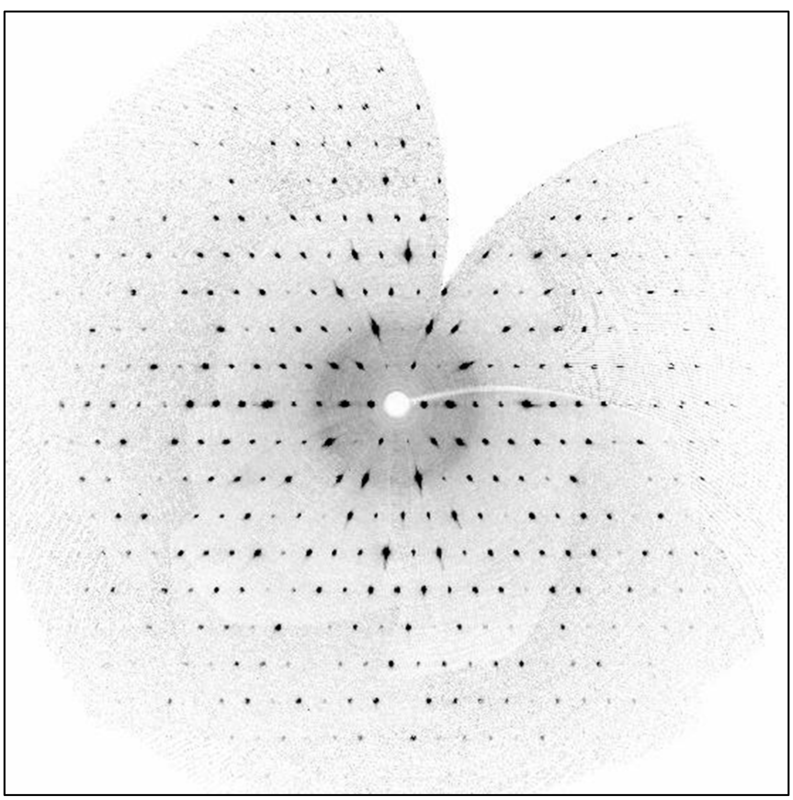
Reciprocal lattice slices for $B2_1$ at 90 K and phase II (indexed in $P2_1/m$) at 233 K

*h*0*l*



$B2_1$ at 90 K

→ **a***

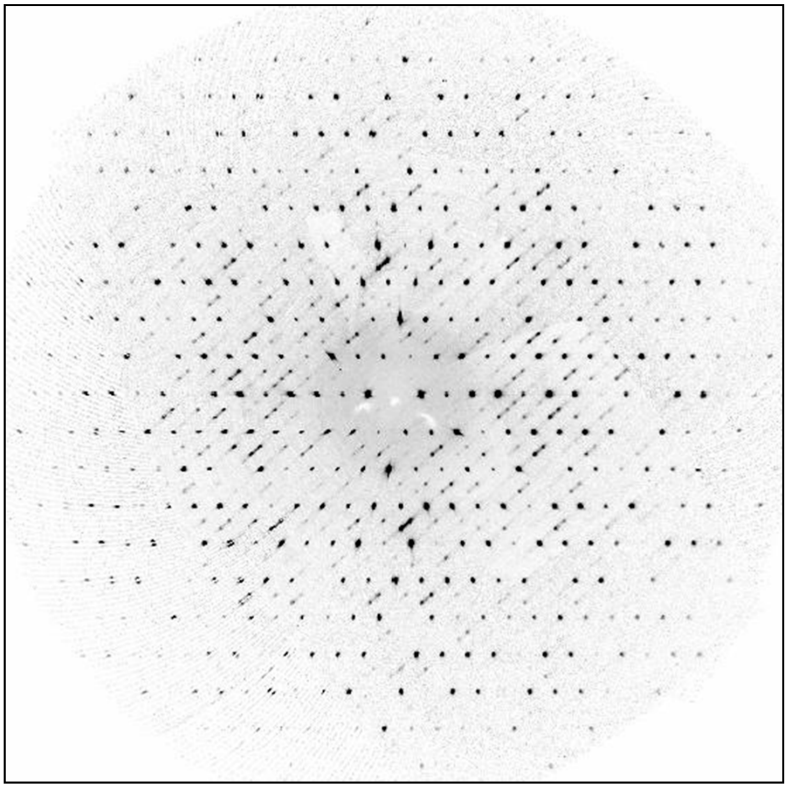


phase II at 233 K

→ **a***

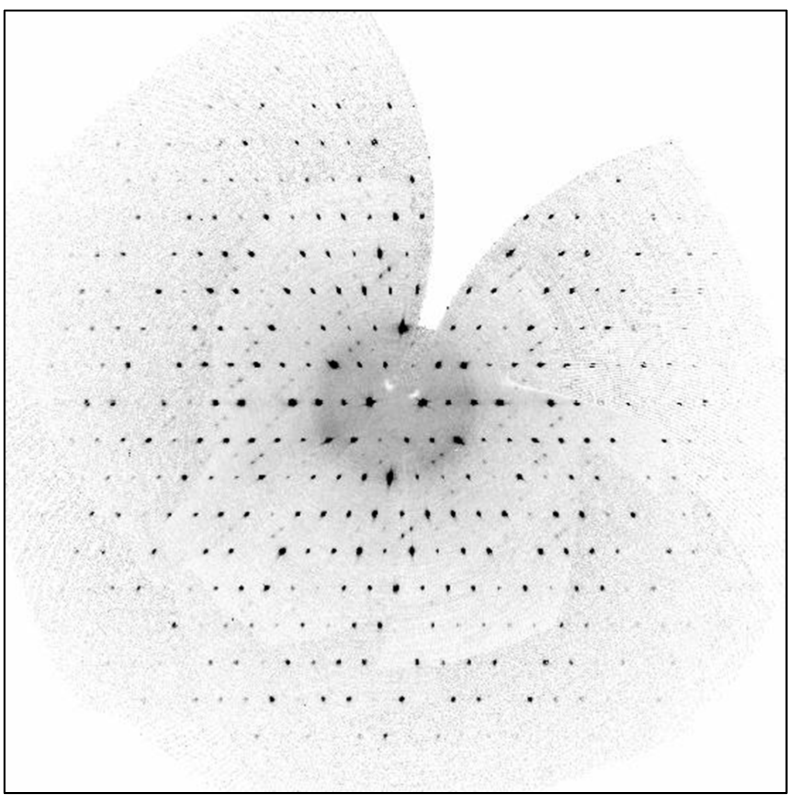
Reciprocal lattice slices for $B2_1$ at 90 K and phase II (indexed in $P2_1/m$) at 233 K

*h*1*l*



$B2_1$ at 90 K

→ **a***

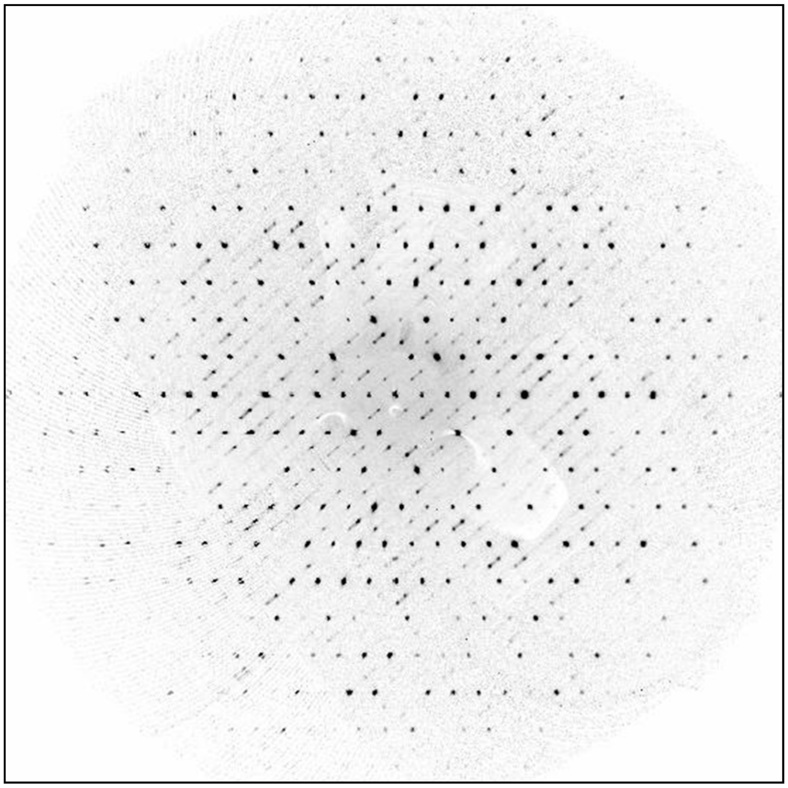


phase II at 233 K

→ **a***

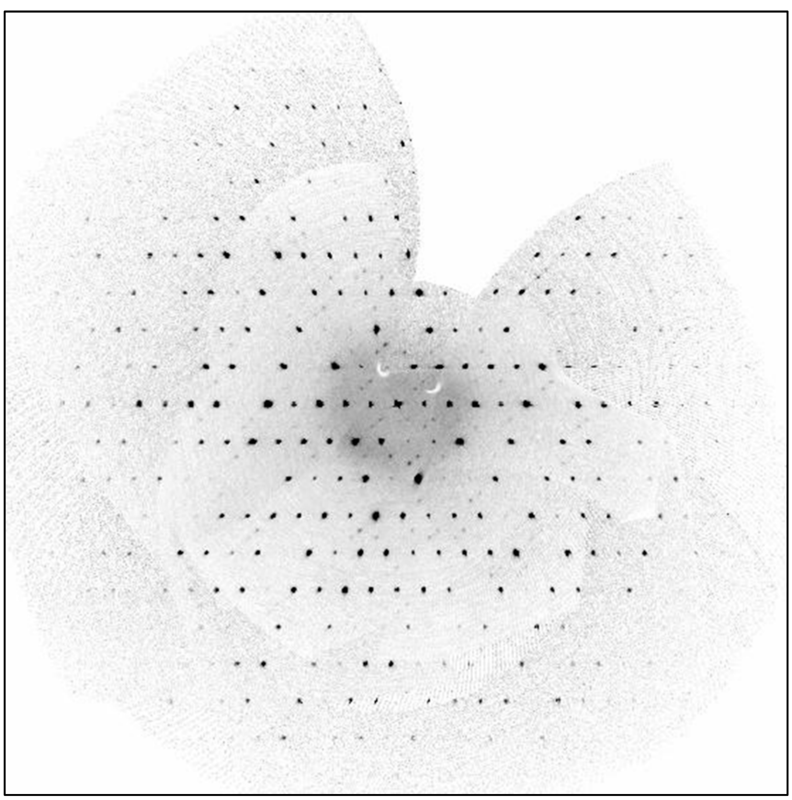
Reciprocal lattice slices for $B2_1$ at 90 K and phase II (indexed in $P2_1/m$) at 233 K

*h*2*l*



$B2_1$ at 90 K

→ **a***

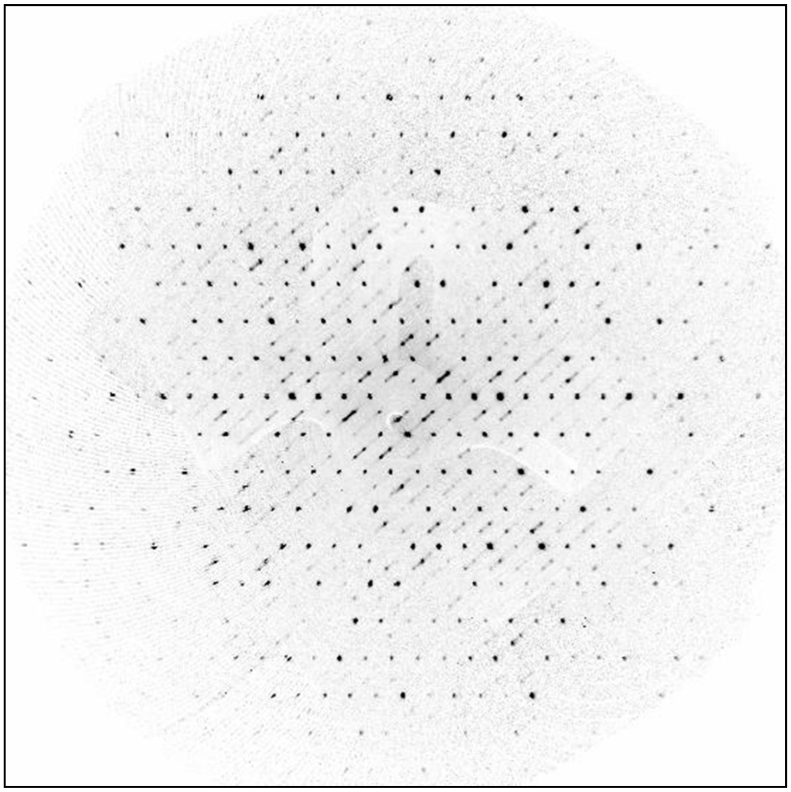


phase II at 233 K

→ **a***

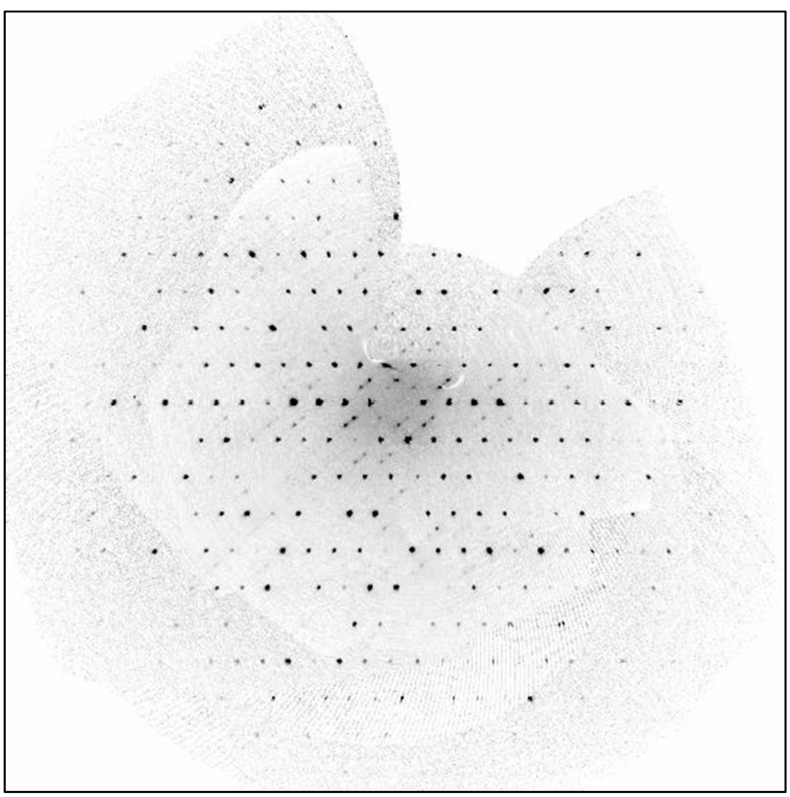
Reciprocal lattice slices for $B2_1$ at 90 K and phase II (indexed in $P2_1/m$) at 233 K

*h*3*l*



$B2_1$ at 90 K

→ **a***

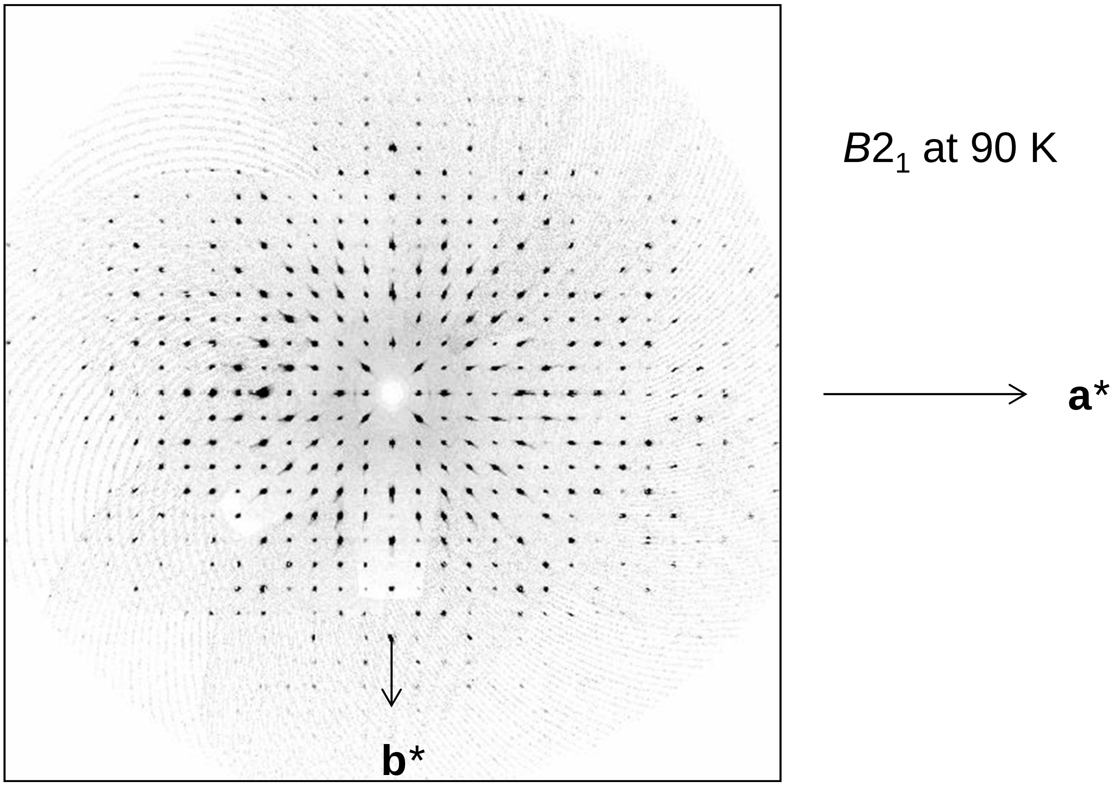


phase II at 233 K

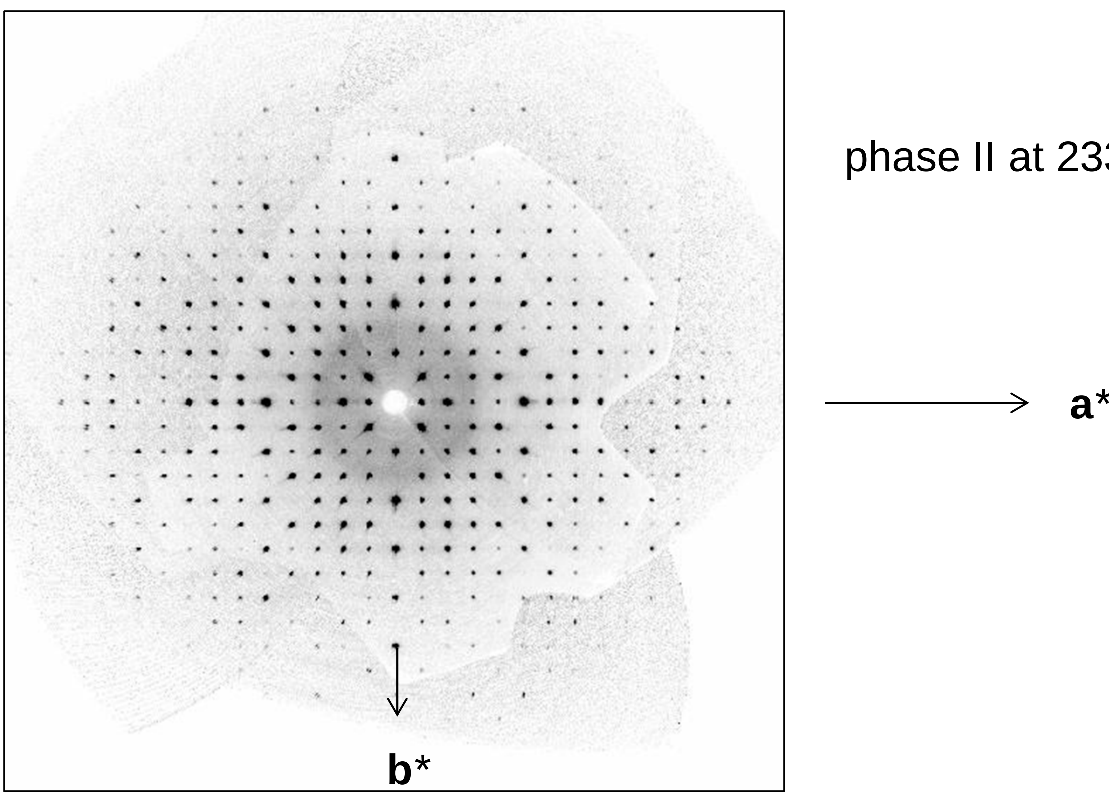
→ **a***

Reciprocal lattice slices for $B2_1$ at 90 K and phase II (indexed in $P2_1/m$) at 233 K

*hk*0



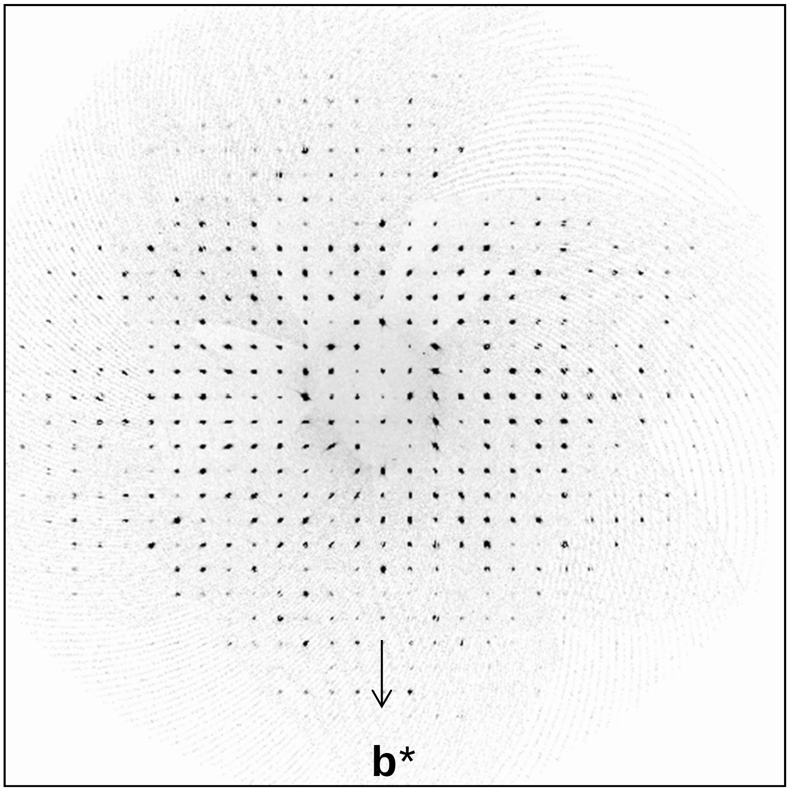

$B2_1$ at 90 K




phase II at 233 K

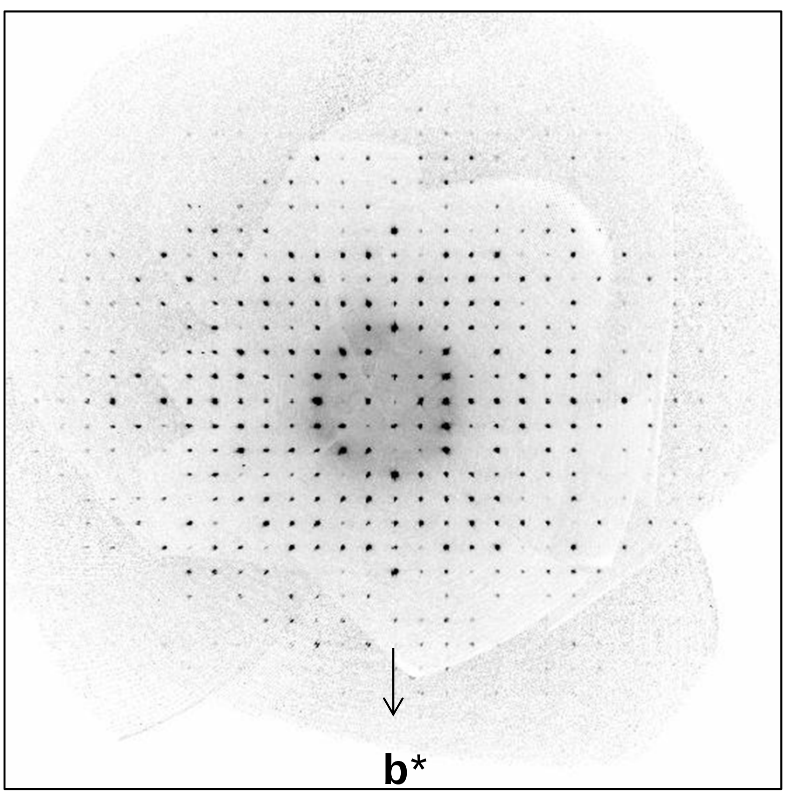
Reciprocal lattice slices for $B2_1$ at 90 K and phase II (indexed in $P2_1/m$) at 233 K

*hk*5 ($B2_1$) and *hk*1 ($P2_1/m$)




$B2_1$ at 90 K

→ **a***



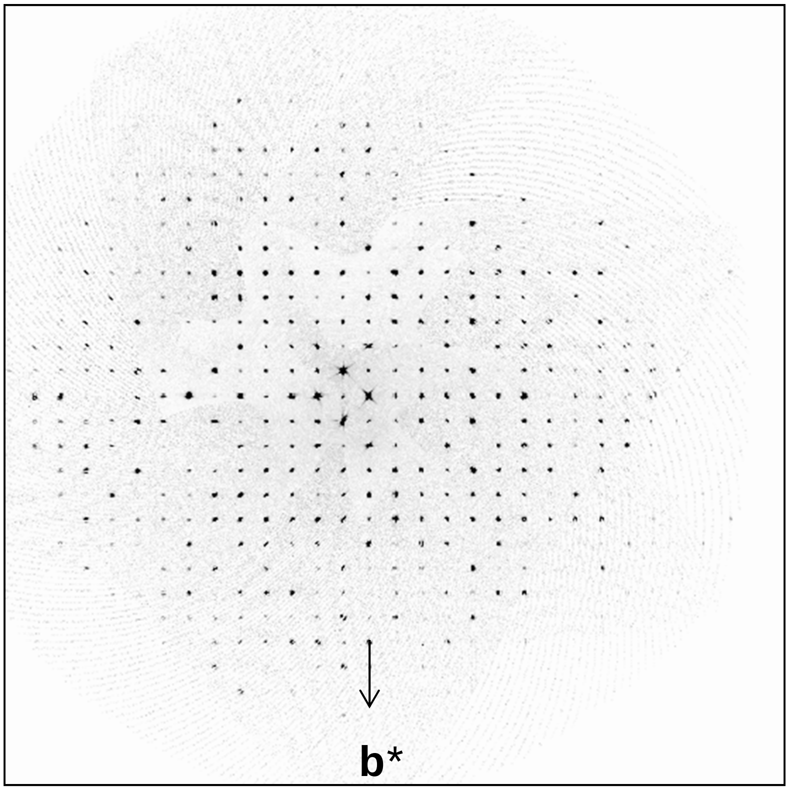

phase II at 233 K

→ **a***

(There is an origin shift along **a*** between the two cells because the two **c*** axes are not parallel)

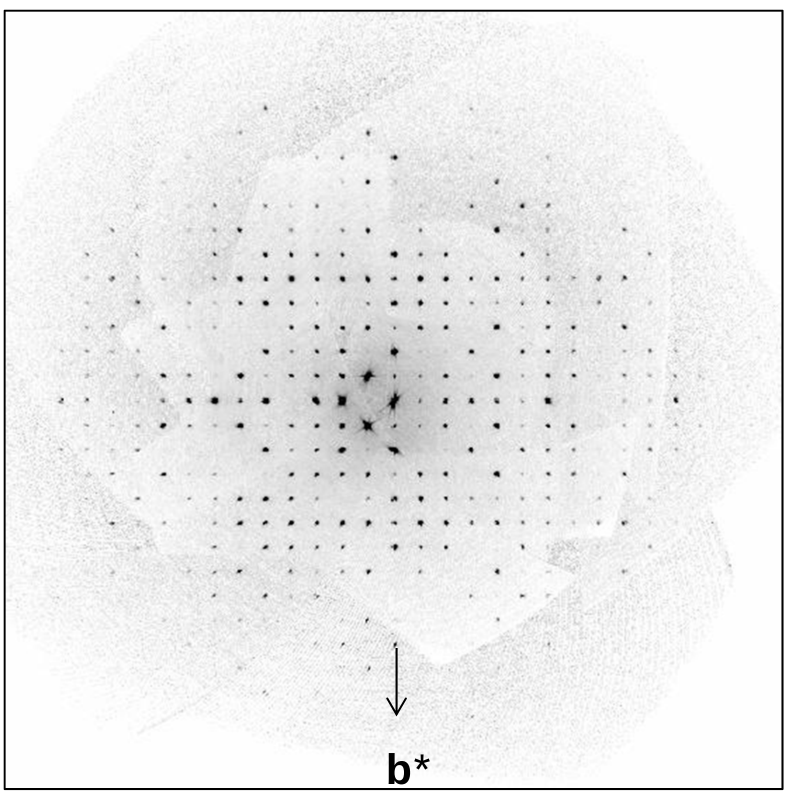
Reciprocal lattice slices for $B2_1$ at 90 K and phase II (indexed in $P2_1/m$) at 233 K

$hk$ 10 ($B2_1$) and $hk2$ ($P2_1/m$)




$B2_1$ at 90 K

**a***



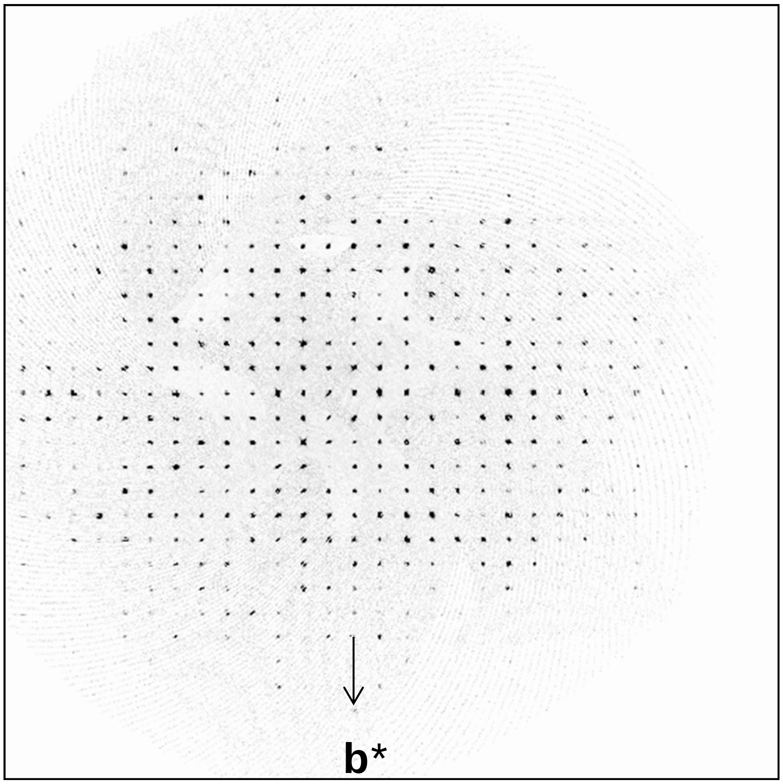

phase II at 233 K

**a***

(There is an origin shift along **a*** between the two cells because the two **c*** axes are not parallel)

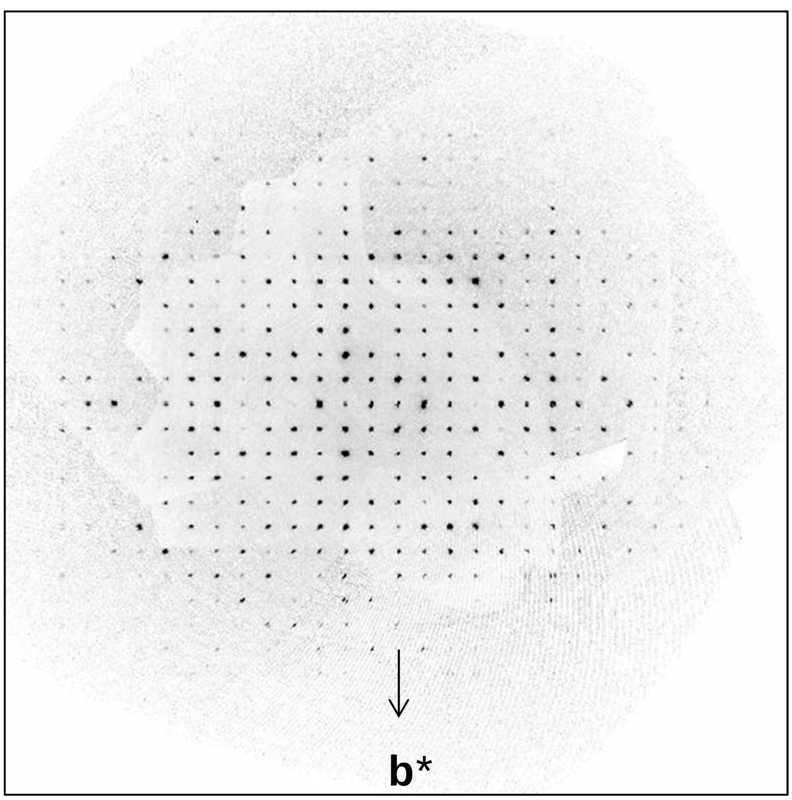
Reciprocal lattice slices for $B2_1$ at 90 K and phase II (indexed in $P2_1/m$) at 233 K

*hk* 15 ($B2_1$) and *hk*3 ($P2_1/m$)




$B2_1$ at 90 K

→ **a***



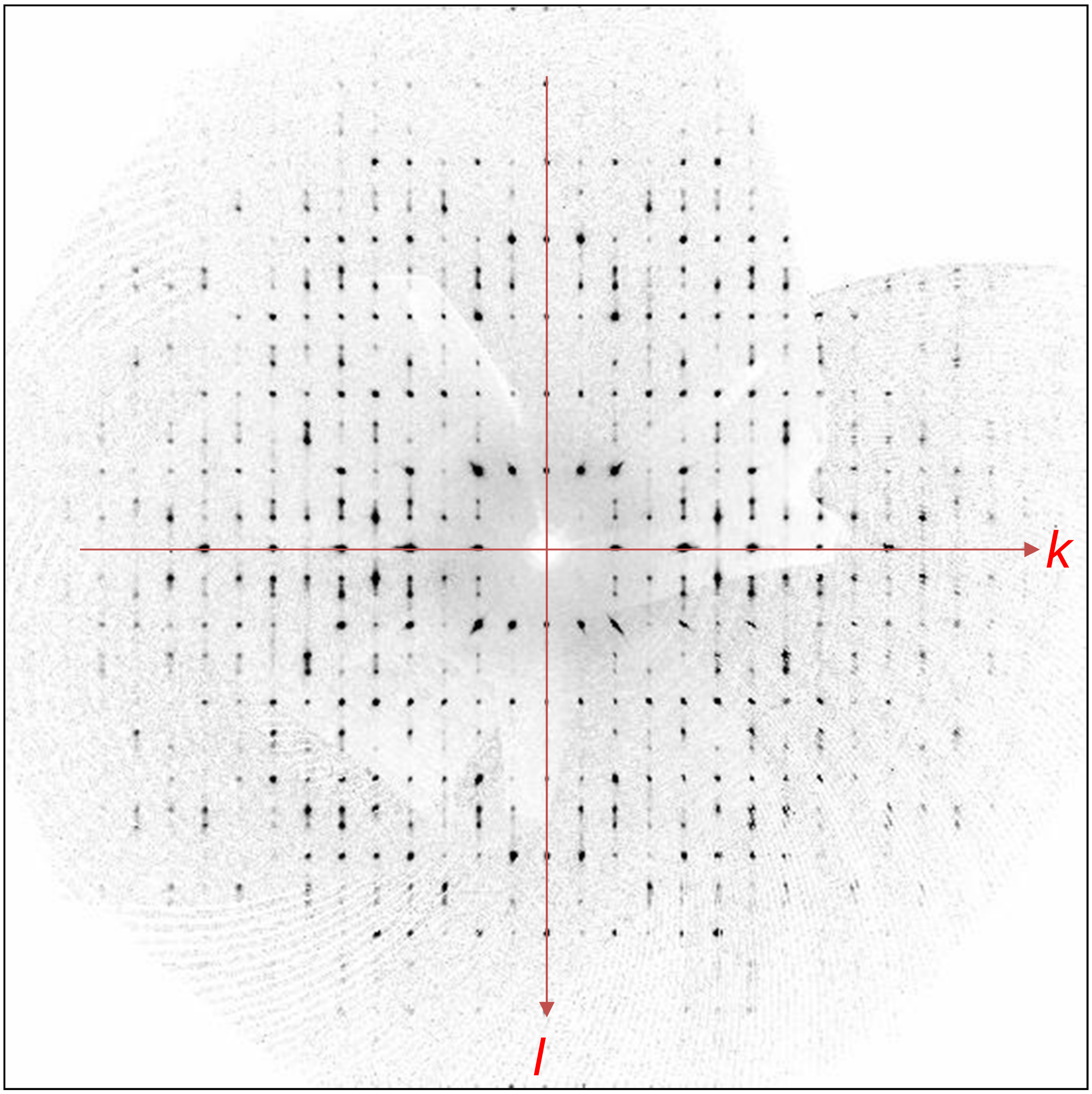

phase II at 233 K

→ **a***

(There is an origin shift along **a*** between the two cells because the two **c*** axes are not parallel)

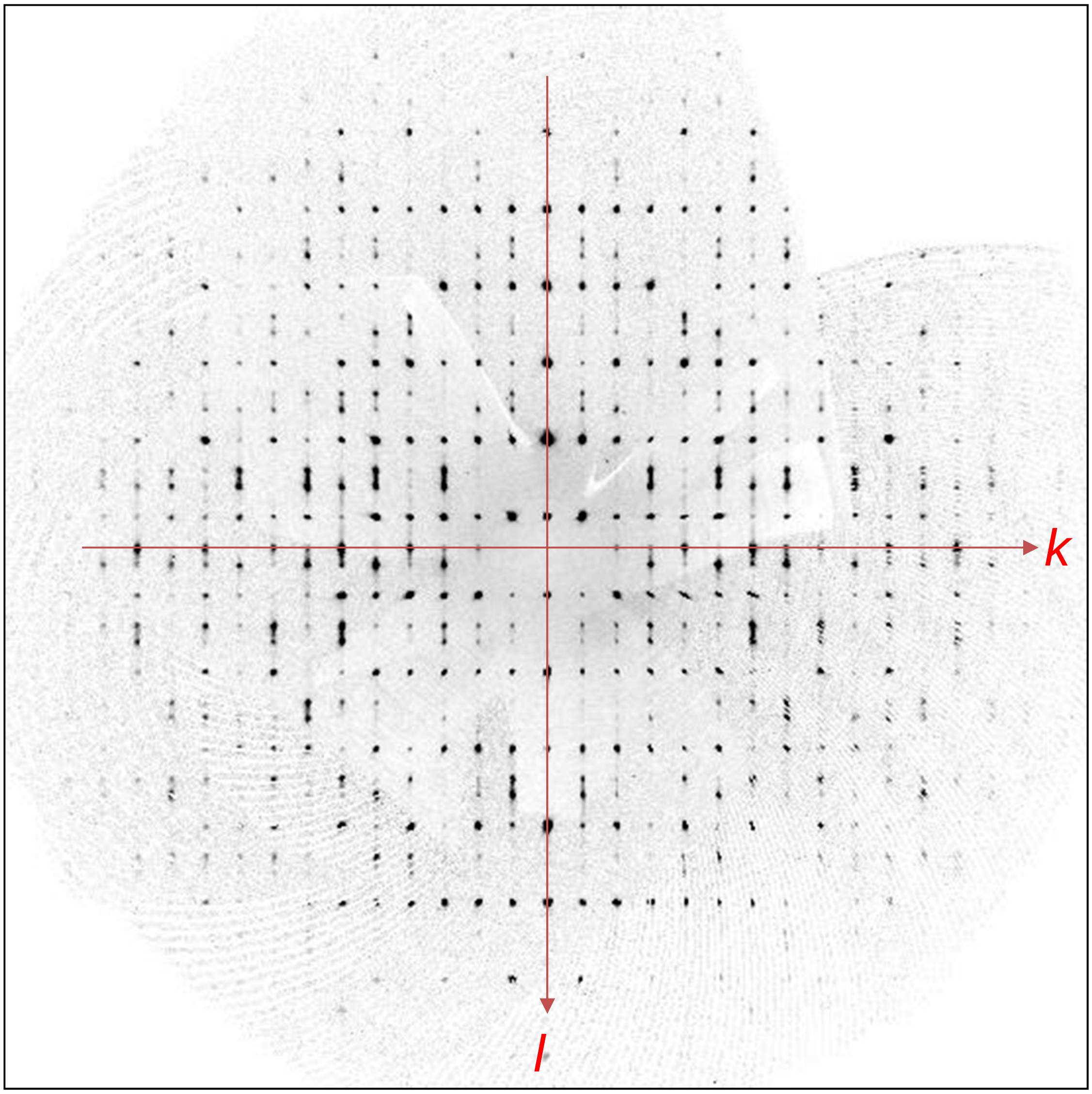
Reciprocal Lattice Slice for $P2_1$ (standard Cell) at 90 K

$0kl$ ($P2_1$ at 90 K)



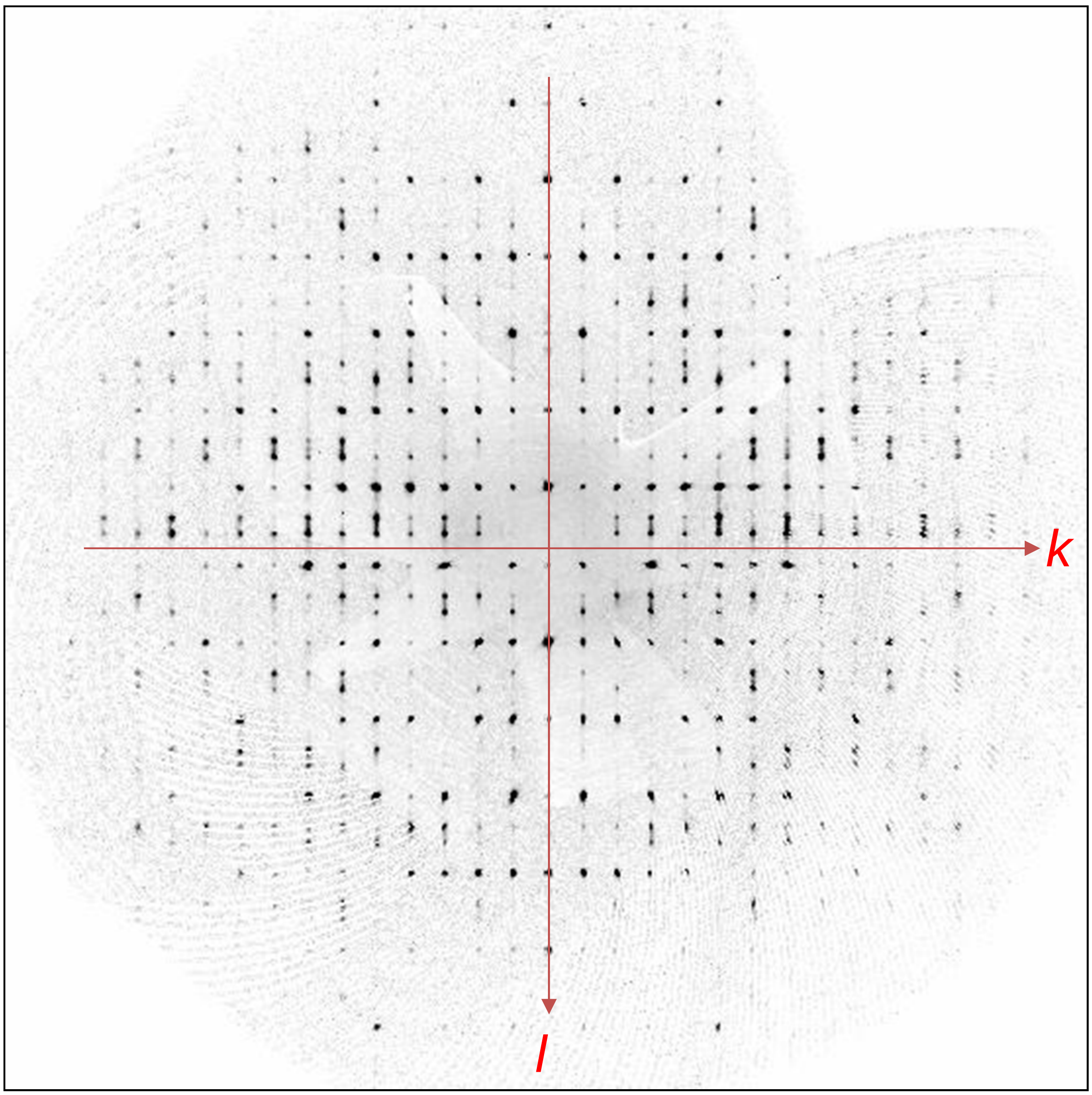
Reciprocal Lattice Slice for $P2_1$ (standard Cell) at 90 K

1*kl* ($P2_1$ at 90 K)



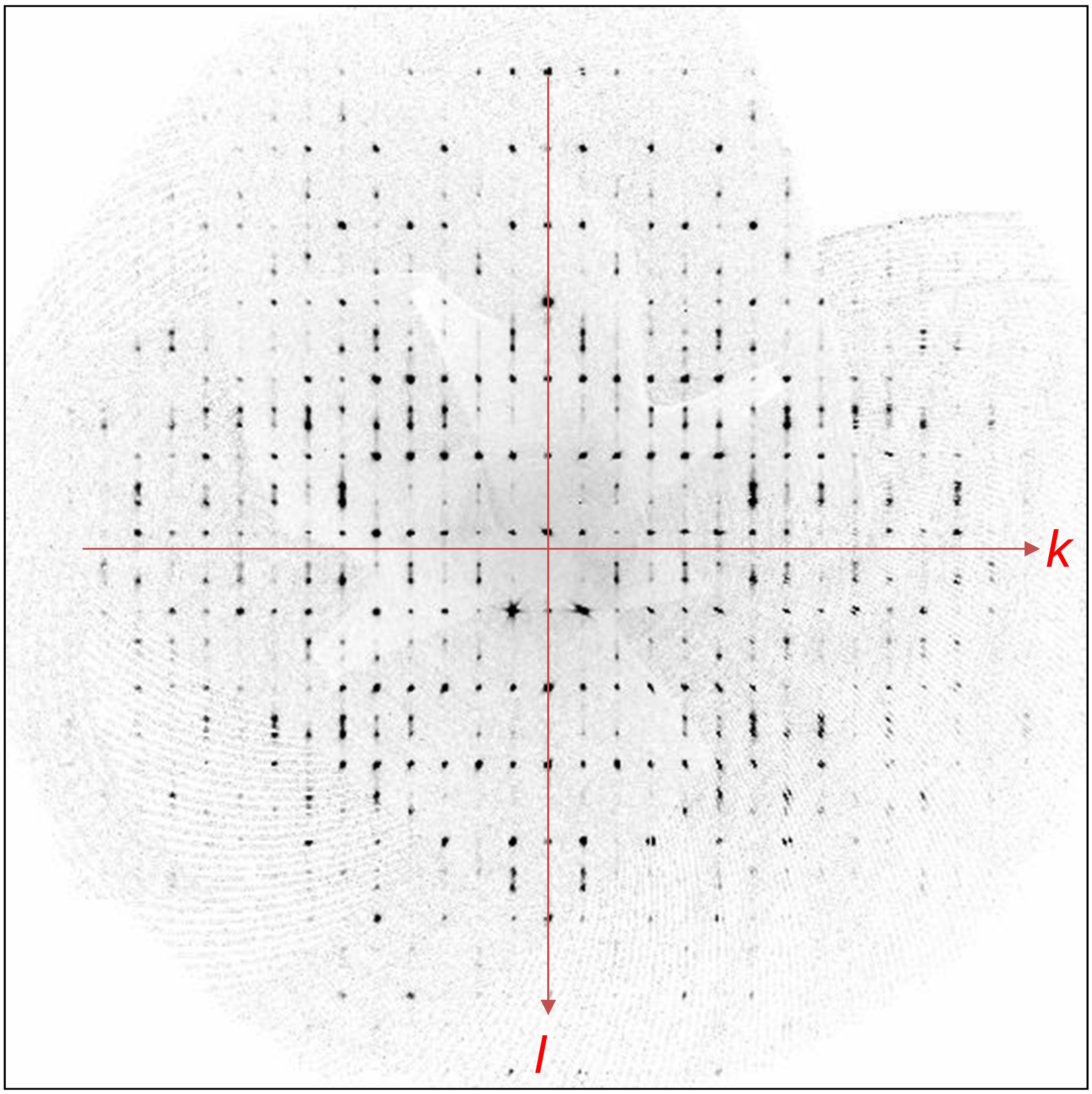
Reciprocal Lattice Slice for $P2_1$ (standard Cell) at 90 K

$2kl$ ($P2_1$ at 90 K)

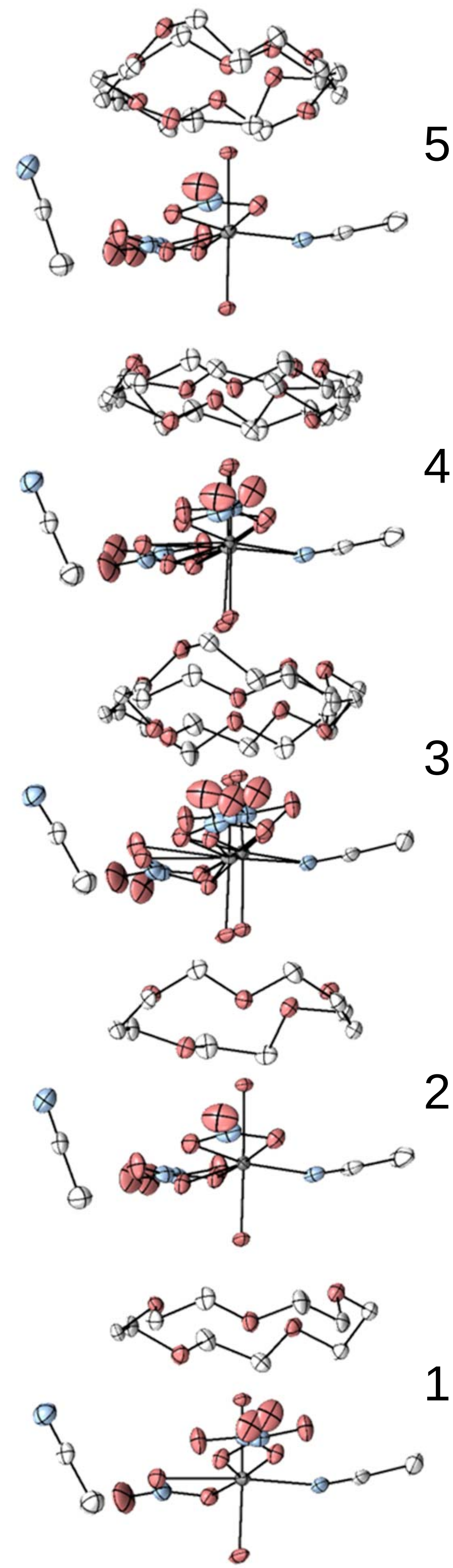


Reciprocal Lattice Slice for $P2_1$ (standard Cell) at 90 K

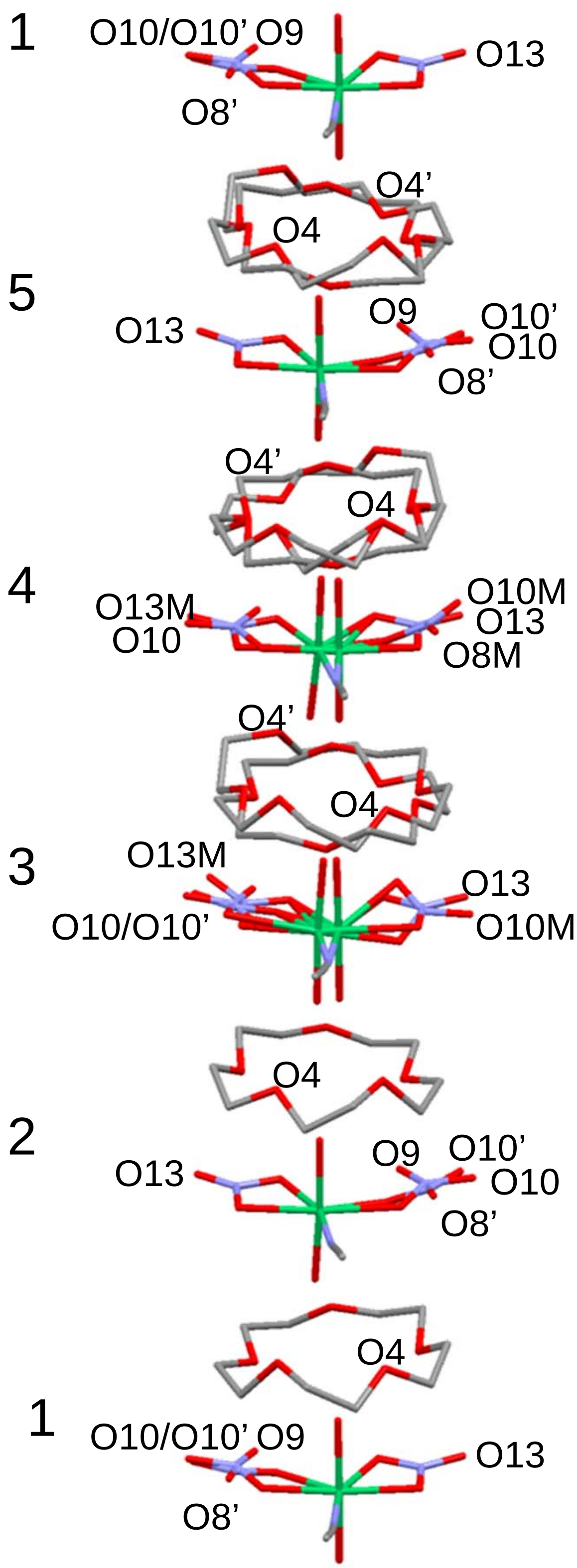
$3kl$ ($P2_1$ at 90 K)



Ellipsoid Plot for
$B2_1$ Structure at 90 K



# $B2_1$ Structure at 90 K




Occupancy Factors
for the major components

O4 0.859(3)

O9 0.785(5)

O4 0.812(3)

O13 0.573(3)
O9 (same)

O4 0.853(2)

O13 0.852(3)
O9 0.312(3)
O8' 0.569(4)
O9M 0.129(4)

O9 0.459(5)

O9 0.707(5)

(All atoms in a $C_{10}H_{20}O_5$ molecule or a $NO_3^-$ ion have the same occupancy factor)

**Description of the disorder in the *B*$2_1$ structure (assumed to be phase II) at 90 K, where the phase is metastable:**

**Ni Complex #1 (contains Ni_1)**

Ordered except for the presence of two orientations of the $\kappa^1 O$ nitrato ligand. In phase III these two orientations are nearly equally probable and in phase I the probabilities are similar (0.56 *vs.* 0.44), but in phase II at 90 K the antiperiplanar orientation (*ap*; N3-Ni-O8-N1 and N3-Ni···N1-O9 torsion angles near 180°) has an occupancy factor of 0.707(5). The occupancy factor for the synperiplanar orientation (*sp*; N3-Ni-O9'-N1' and N3-Ni···N1'-O8' torsion angles < 30°) is 0.293(5).

**15-Crown-5 #1 (*i.e.*, 15C5_1)**

Ordered.

**Ni Complex #2 (contains Ni_2)**

Ordered except for the presence of two orientations of the $\kappa^1 O$ nitrato ligand. The *ap* orientation has an occupancy factor of 0.459(5).

**15-Crown-5 #2 (*i.e.*, 15C5_2)**

Ordered

**Ni Complex #3 (contains Ni_3)**

Disorder of the $\kappa^1 O$ and $\kappa^2 O$ nitrato ligands; two positions of the $H_2O$-Ni-$OH_2$ unit; occupancy factor for the $\kappa^2 O$ nitrato related to the corresponding ligand in Ni complex #2 by the pseudoglide is 0.852(3). Occupancy factors for the two $H_2O$-Ni-$OH_2$ units were tied to those of $\kappa^1 O/\kappa^2 O$ nitrato disorder so as to preserve the Ni-O distances found in ordered complexes. Two orientations of the $\kappa^1 O$ nitrato ligand were found on the side of greater overall occupancy [0.312 and 0.560(3) for *ap* and *sp*] but only one orientation (*ap*) could be identified on the other. The occupancy factors for the three $\kappa^1 O$ nitrato ligands sum to 1.001, but they do not quite match the occupancy factors for the two positions of the $\kappa^2 O$ ligand [0.312+0.560 = 0.852(4) *vs.* 0.872(3)]. This complicated model was, however, the best that could be found.

**15-Crown-5 #3 (*i.e.*, 15C5_3)**

Two orientations of the ring as in phase I. The occupancy factor for the major component is 0.853(2).

**Ni Complex #4 (contains Ni_4)**

Disorder of the $\kappa^1 O$ and $\kappa^2 O$ nitrato ligands; two positions of the $H_2O$-Ni-$OH_2$ unit; occupancy factors are close to ½ [*i.e.*, 0.573/0.427(3)]. The occupancy factors of the *ap* and *sp* orientations of the κ$^1$*O* nitrato ligand (one found on one side of the pseudomirror and one on the other) were set equal to the occupancy factor for the corresponding κ$^2$*O* nitrato ligand.

**15-Crown-5 #4 (*i.e.*, 15C5_4)**

Two orientations of the ring as in phase I. The occupancy factor for the major component is 0.812(3).

**Ni Complex #5 (contains Ni_5)**

Ordered except for the presence of two orientations of the κ$^1$*O* nitrato ligand. The *ap* orientation has an occupancy factor of 0.785(4).

**15-Crown-5 #5 (*i.e.*, 15C5_5)**

Two orientations of the ring as in phase I. The occupancy factor for the major component is 0.859(3).

The alternation of the κ$^1$*O*/κ$^2$*O* nitrato ligands found in phase III is found in Ni complexes #5, #1, and #2. It is less perfect in #3 [occupancy factors 0.852/0.148(3) rather than 1/0], and is essentially absent in #4 [occupancy factors 0.573/0.427(3)]. An odd number of independent complexes in the chain (here, 5) guarantees that the alternation must fail at some point (here, at Ni complex #4).

In phases I and III the occupancy factors for the two orientation of the κ$^1$*O* nitrato ligand are roughly equal. In phase II the occupancies are quite near ½ for complexes #2, #3, and #4, but the *ap* orientation is clearly more favorable for complexes #5 and #1 [occupancy factors 0.785(4) and 0.707(5)].

Two of the 15-crown-5 molecules (#1 and #2) are completely ordered, as they are in phase III. The other three are more ordered than in phase I [occupancy factors for major component 0.852(2), 0.812(3), and 0.859(3) in phase II *vs.* 0.667(3) in phase I].

**Cell constants determined for the basic cell ($P2_1/m$, $Z' = ½$) of phase II within its range of stability:**

| ***T*** (K) | ***a*** (Å) | ***b*** (Å) | ***c*** (Å) | ***β*** (°) | ***V*** (Å$^3$) |
|---|---|---|---|---|---|
| 233 (1st *T* sequence) | 12.133 | 12.321 | 8.133 | 105.51 | 1171.4 |
| 239 (2nd *T* sequence) | 12.131 | 12.334 | 8.140 | 105.51 | 1173.5 |
| 236 (2nd *T* sequence) | 12.132 | 12.327 | 8.137 | 105.51 | 1172.6 |
| 233 (2nd *T* sequence) | 12.136 | 12.316 | 8.131 | 105.50 | 1171.0 |