

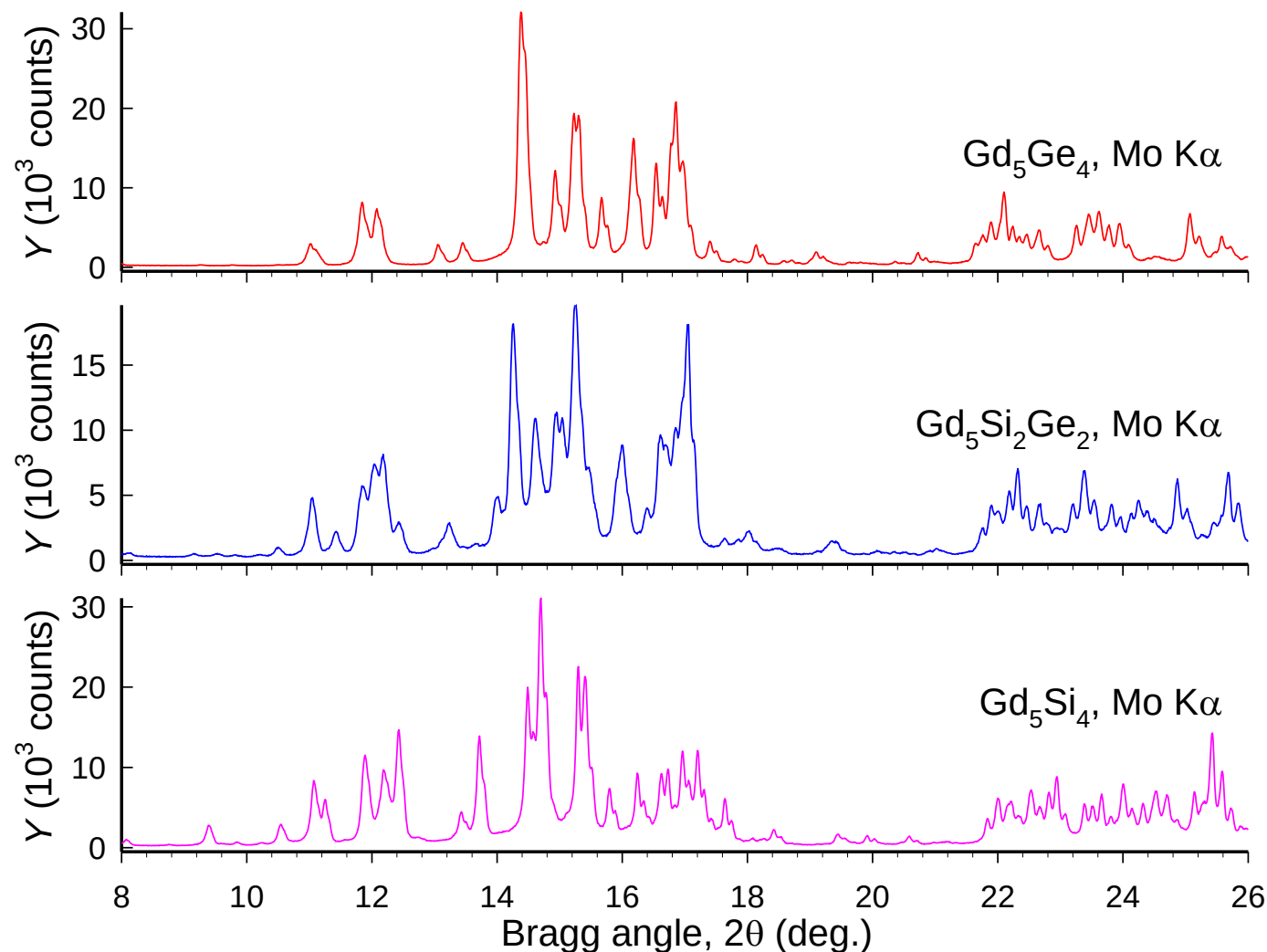
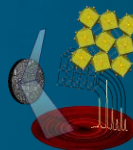


Figure 19.1. Low Bragg angle regions of the powder diffraction patterns of Gd_5Ge_4 , $Gd_5Si_2Ge_2$, and Gd_5Si_4 . The three patterns are representative for materials in the Gd_5Ge_4 -based solid solution, the intermediate intermetallic phase, and the Gd_5Si_4 -based solid solution, respectively. Distinct clusters of Bragg peaks observed in the regions $\sim 10 < 2\theta < \sim 18^\circ$ and $\sim 21 < 2\theta < \sim 26^\circ$ point to close relationships between the three crystal structures. Gradual redistribution of peak intensities from one pattern to another, however, cannot be solely associated with the expected change in lattice parameters due to the substitution of smaller Si for larger Ge atoms. Therefore, we conclude that three crystal structures are closely related, yet different.

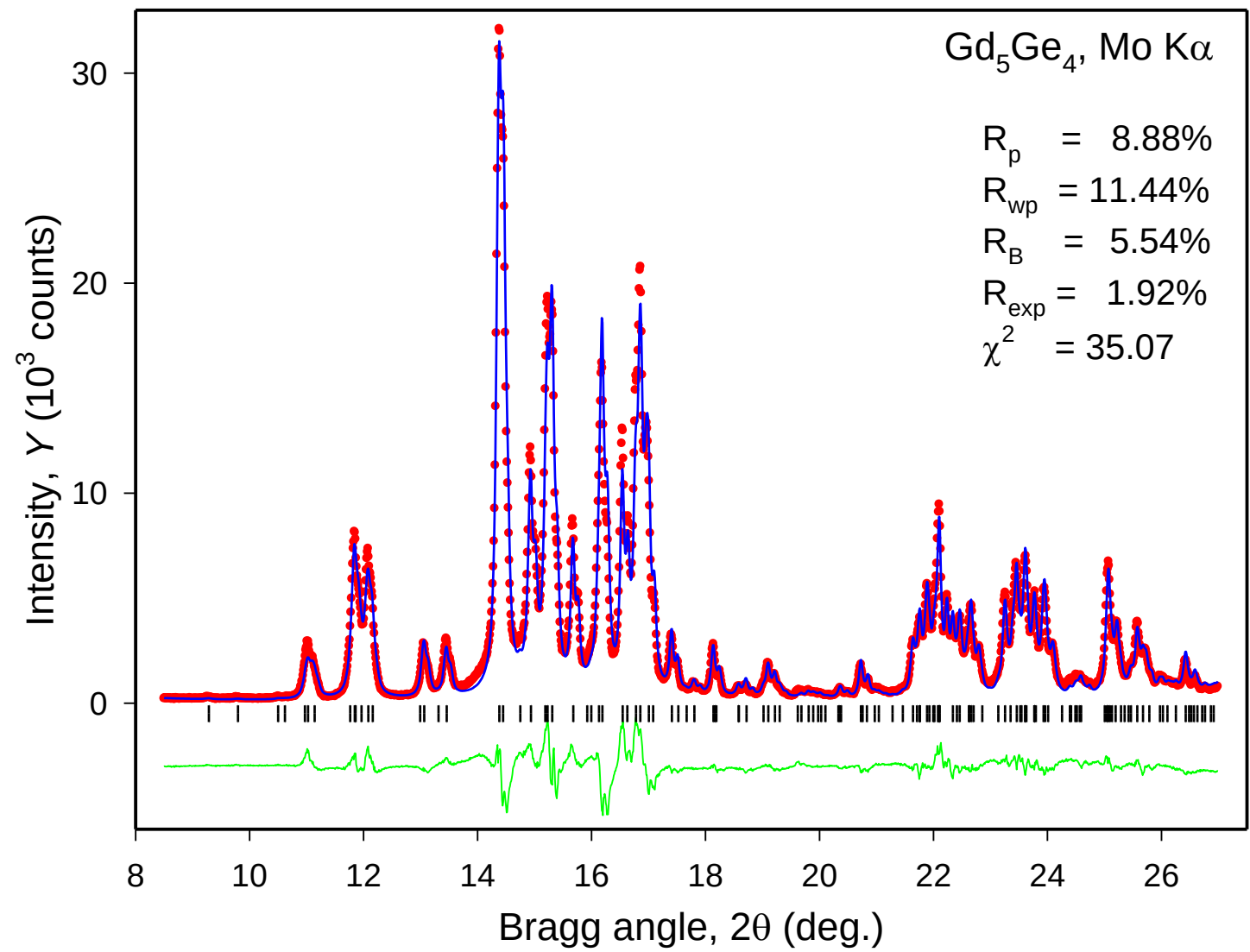
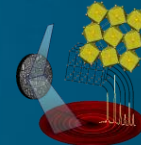


Figure 19.2. The observed and calculated intensities in a fragment of a powder diffraction pattern of Gd_5Ge_4 . The calculated intensity has been scaled to match the observed profile.

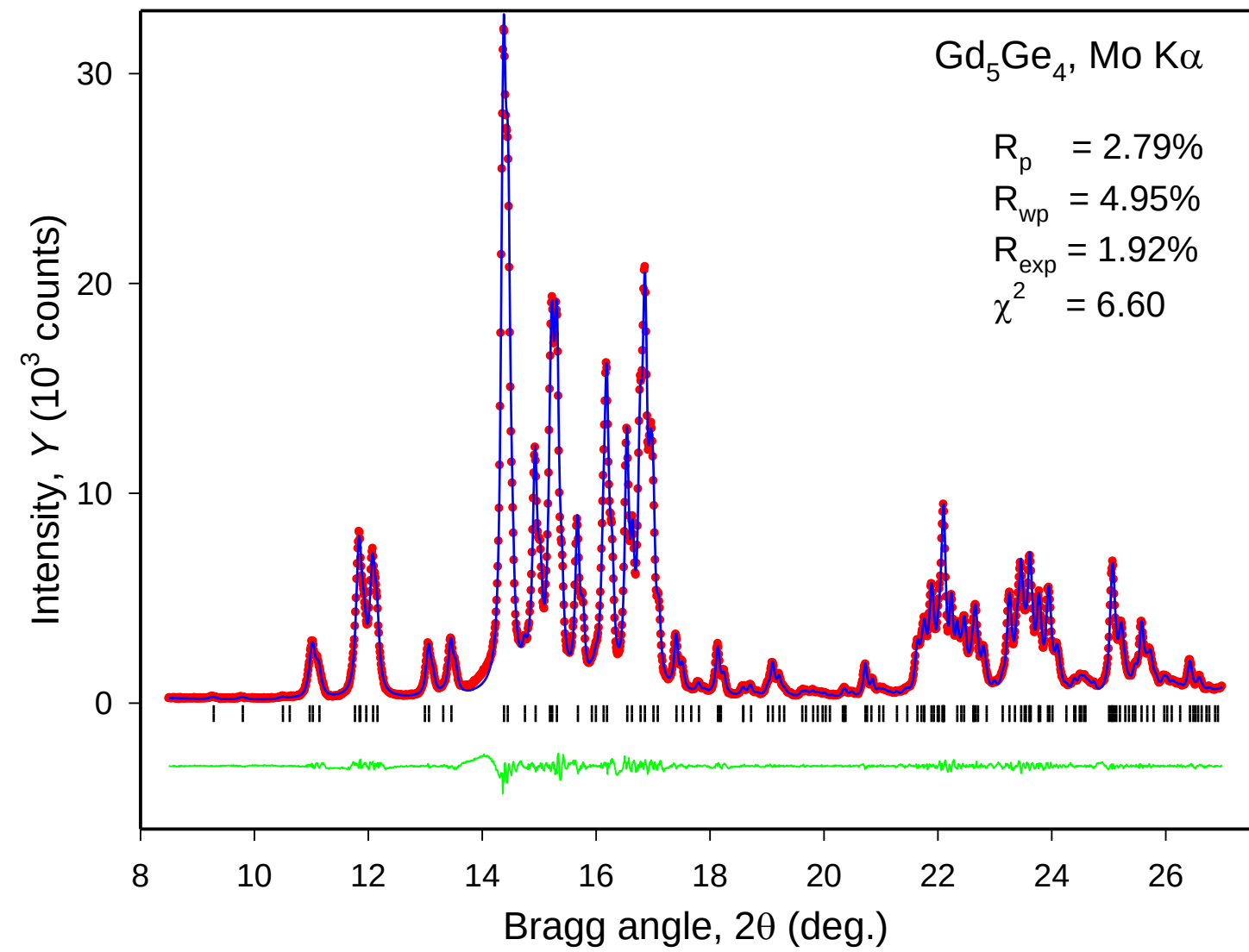
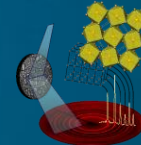


Figure 19.3. The results of Le Bail’s full pattern decomposition of the powder diffraction pattern of Gd_5Ge_4 . The discrepancies between the observed and calculated profiles are small and all residuals are low, indicating that the unit cell dimensions are accurately determined and that the chosen peak-shape function (pseudo-Voigt) is a good choice for this experiment.

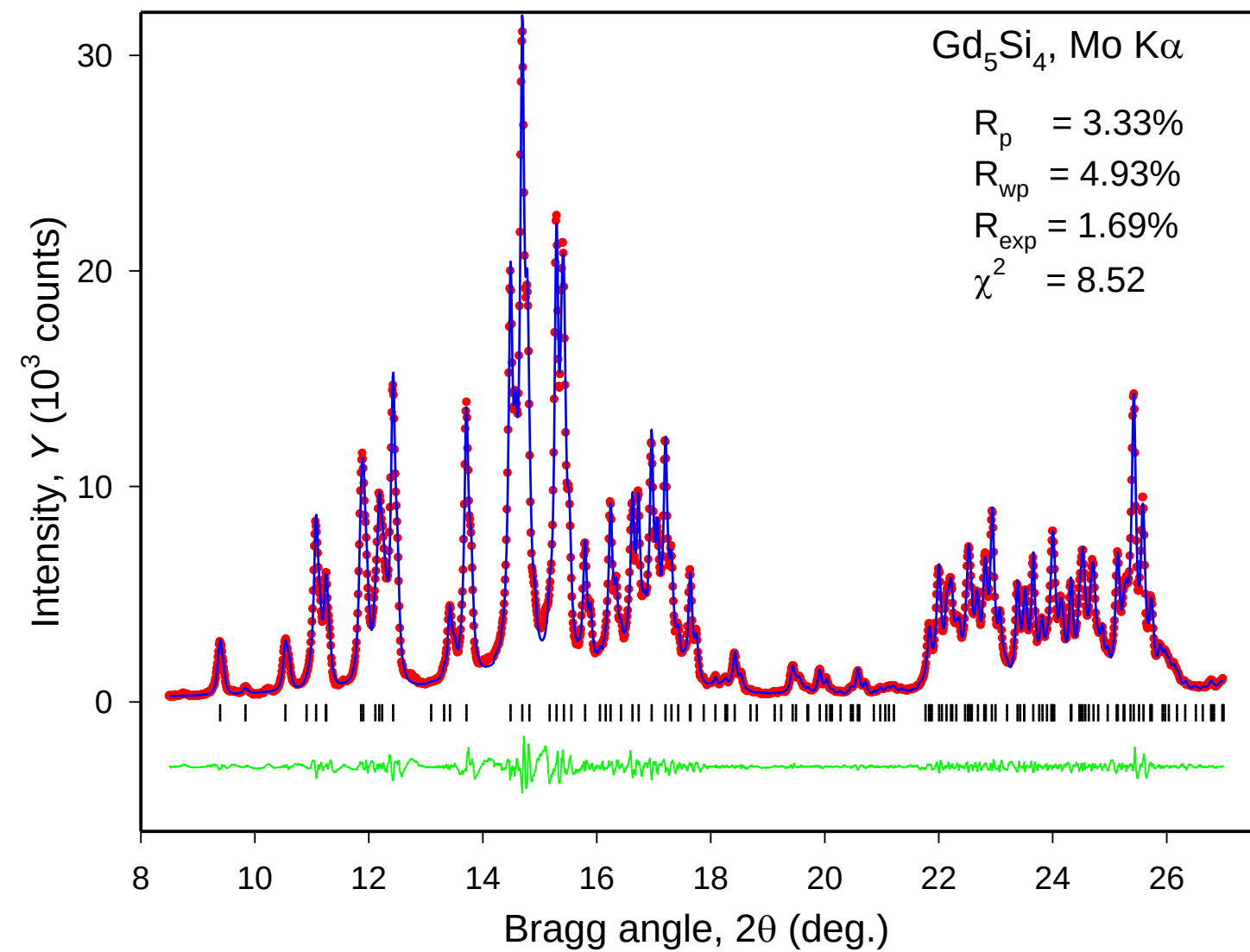
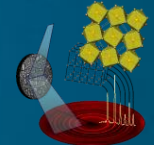


Figure 19.4. The results of Le Bail’s full pattern decomposition of the powder diffraction pattern of Gd_5Si_4 . The discrepancies between the observed and calculated profiles are small and all residuals are low, indicating that the unit cell dimensions are accurately determined and that the chosen peak-shape function (Pearson-VII) is a good choice for this experiment.

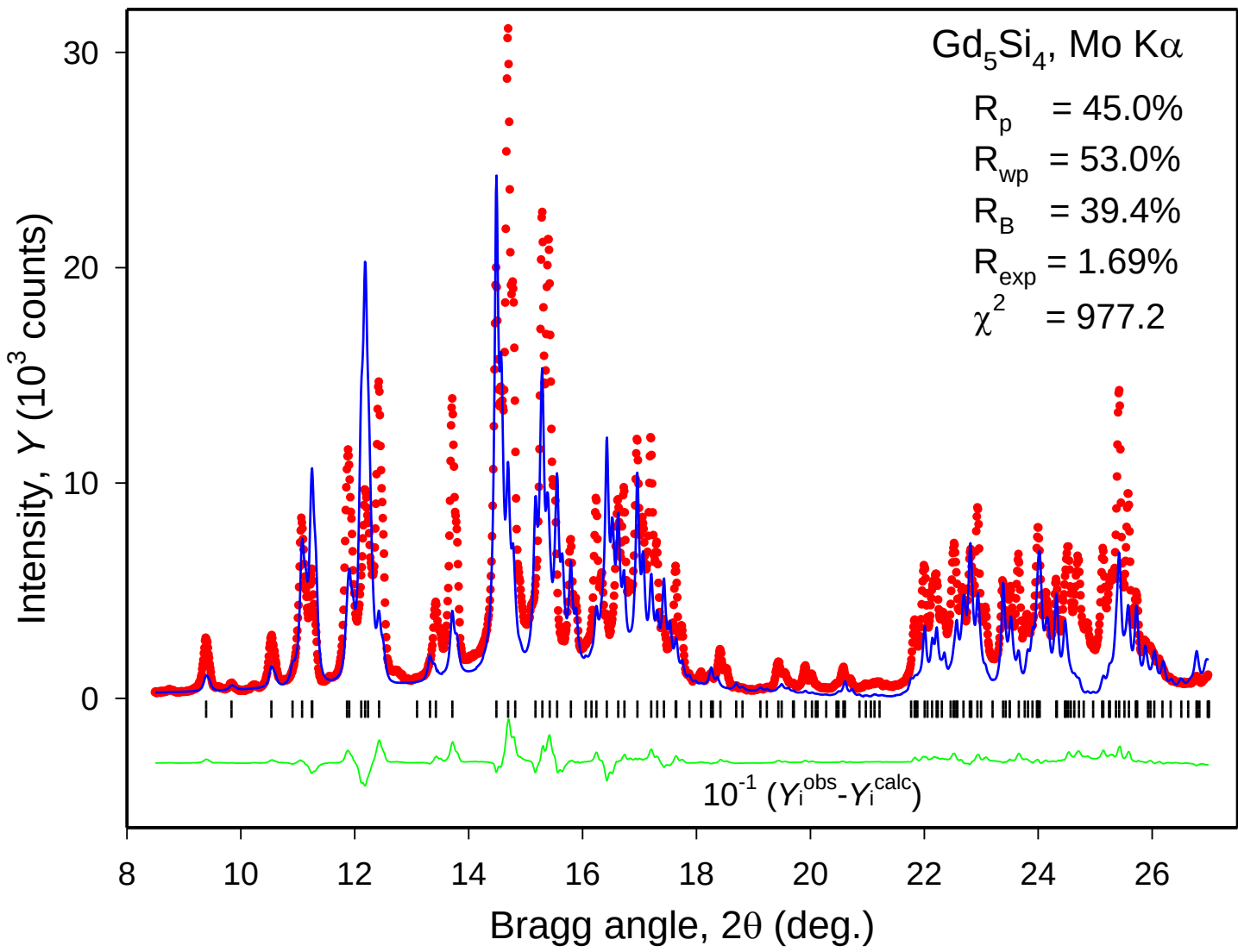
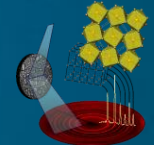


Figure 19.5. The observed (*circles*) and calculated (*lines*) intensities in a fragment of powder diffraction pattern of Gd₅Si₄. The calculated intensity has been normalized to match the observed profile. Peak-shape, background and lattice parameters employed to compute the calculated profile have been obtained by a full pattern decomposition of the observed data using Le Bail’s technique, as shown in Figure 19.4. Note, that the difference plot has been compressed tenfold for clarity.

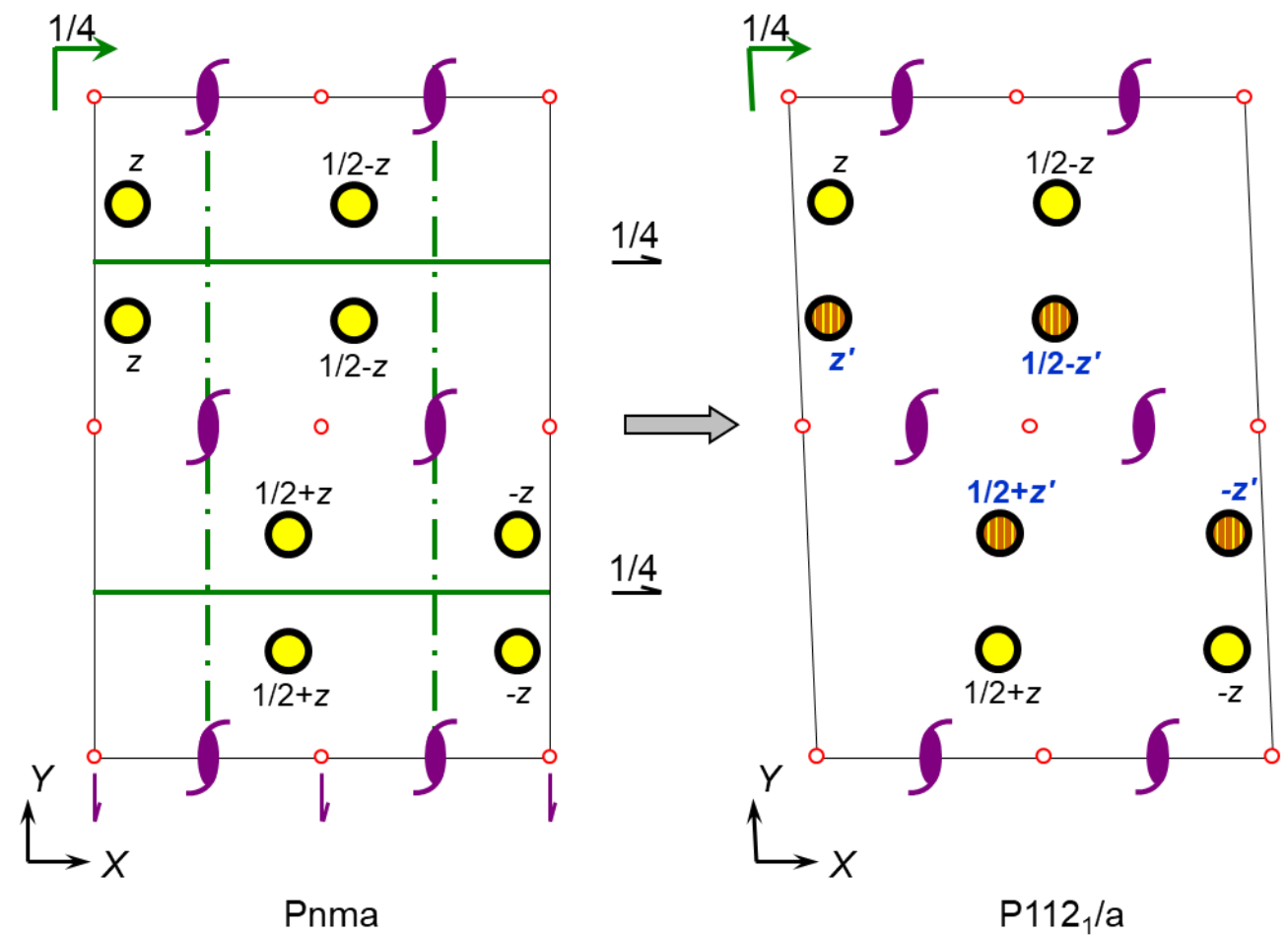
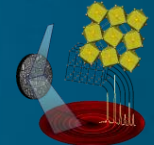


Figure 19.6. The disappearance of *mirror planes*, m , and *glide planes*, n , during a monoclinic distortion of the orthorhombic unit cell corresponding to the space group symmetry $Pnma$ (*left*) when the angle between a and b unit cell edges deviates from 90° (*right*). The resulting space-group symmetry is $P112_1/a$: centers of inversion, twofold screw axes perpendicular to the XY plane, and glide planes, a , parallel to the XY plane remain unaffected by this distortion. The *open circles* on the left represent symmetrically equivalent atoms located in a general site position, 8(d), in the space group $Pnma$. The eightfold site splits into two independent 4(e) fourfold sites in the space group symmetry $P112_1/a$, as indicated by both open and hatched circles on the right, for which $z' \cong z$.

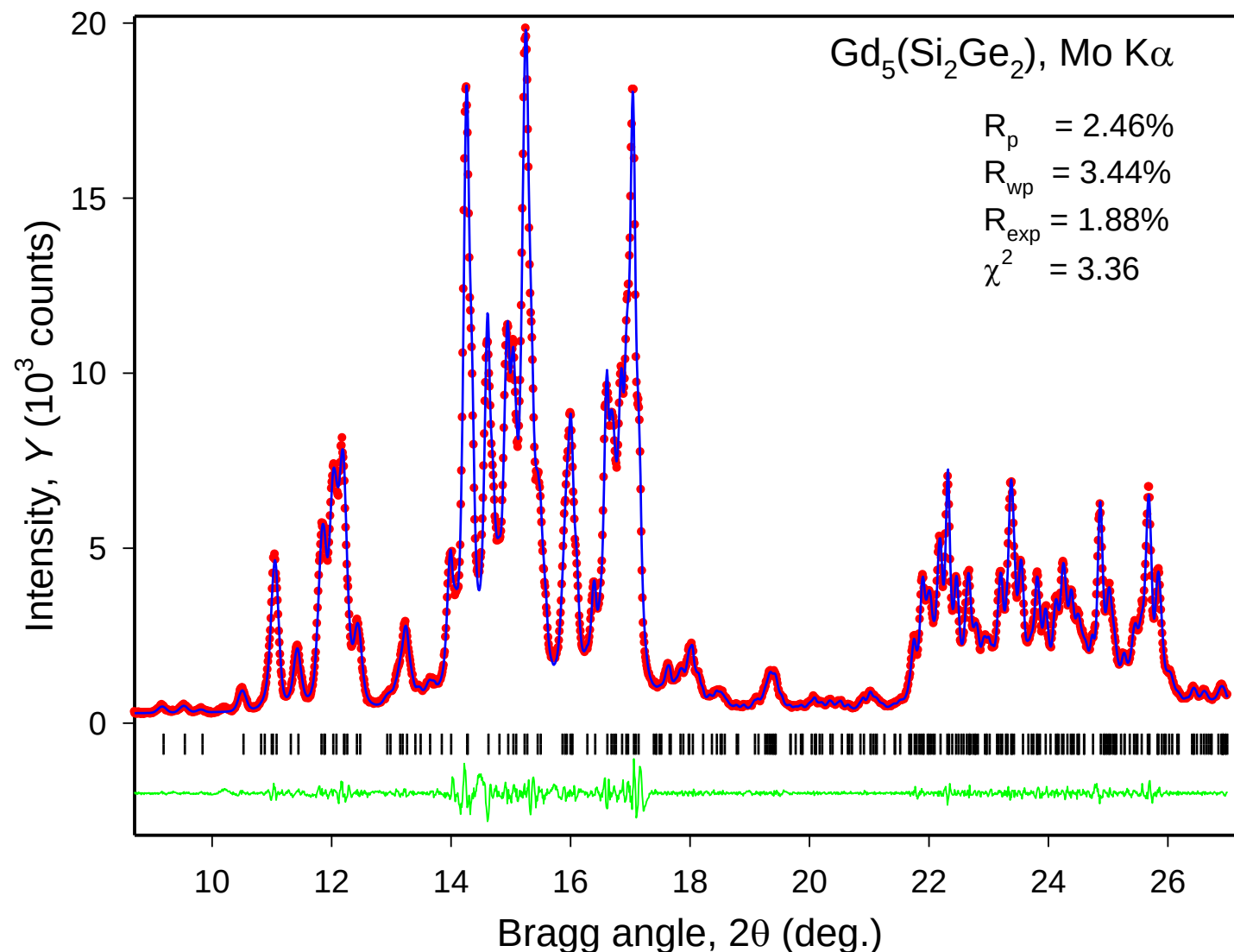
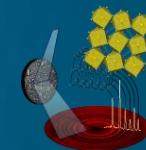


Figure 19.7. The results of Le Bail's full pattern decomposition of the powder diffraction pattern of $\text{Gd}_5\text{Si}_2\text{Ge}_2$. The discrepancies between the observed and calculated profiles are small and all residuals are low, indicating that the unit cell dimensions are accurately determined and that the chosen peak-shape function (pseudo-Voigt) is a good choice for this experiment.

The observed data are available in the data files *Ch19Ex03_MoKa.xy* and *Ch19Ex03_MoKa.dat* online.

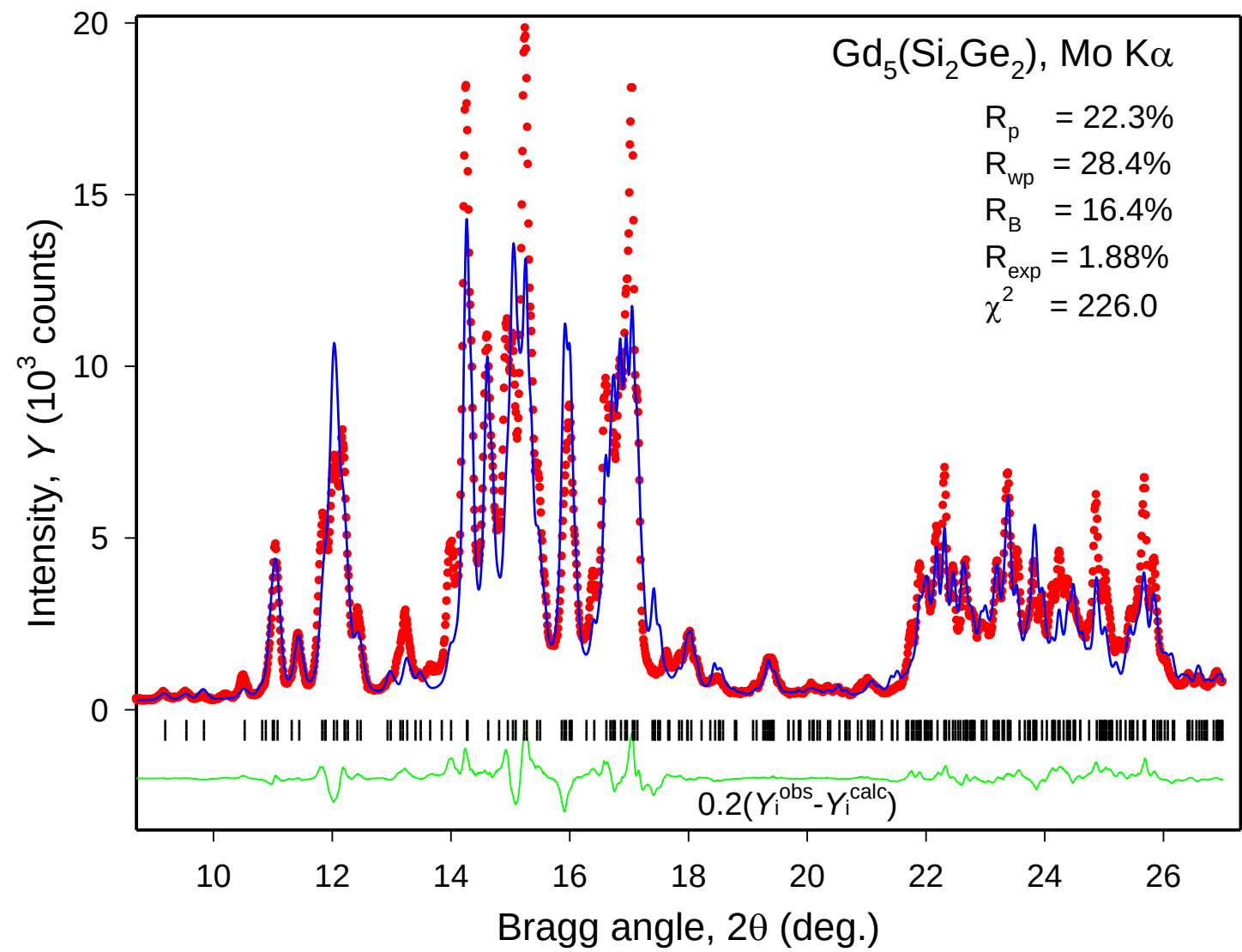
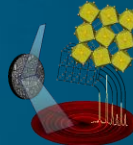


Figure 19.8. The observed (*circles*) and calculated (*lines*) intensities in a fragment of powder diffraction pattern of $\text{Gd}_5\text{Si}_2\text{Ge}_2$. The calculated intensity has been normalized to match the observed profile. Peak-shape, background and lattice parameters employed to compute the calculated profile have been obtained by a full pattern decomposition of the observed data using Le Bail’s technique, as shown in Figure 19.7. Note, that the difference plot has been compressed fivefold for clarity (the differences are too large to be well seen).

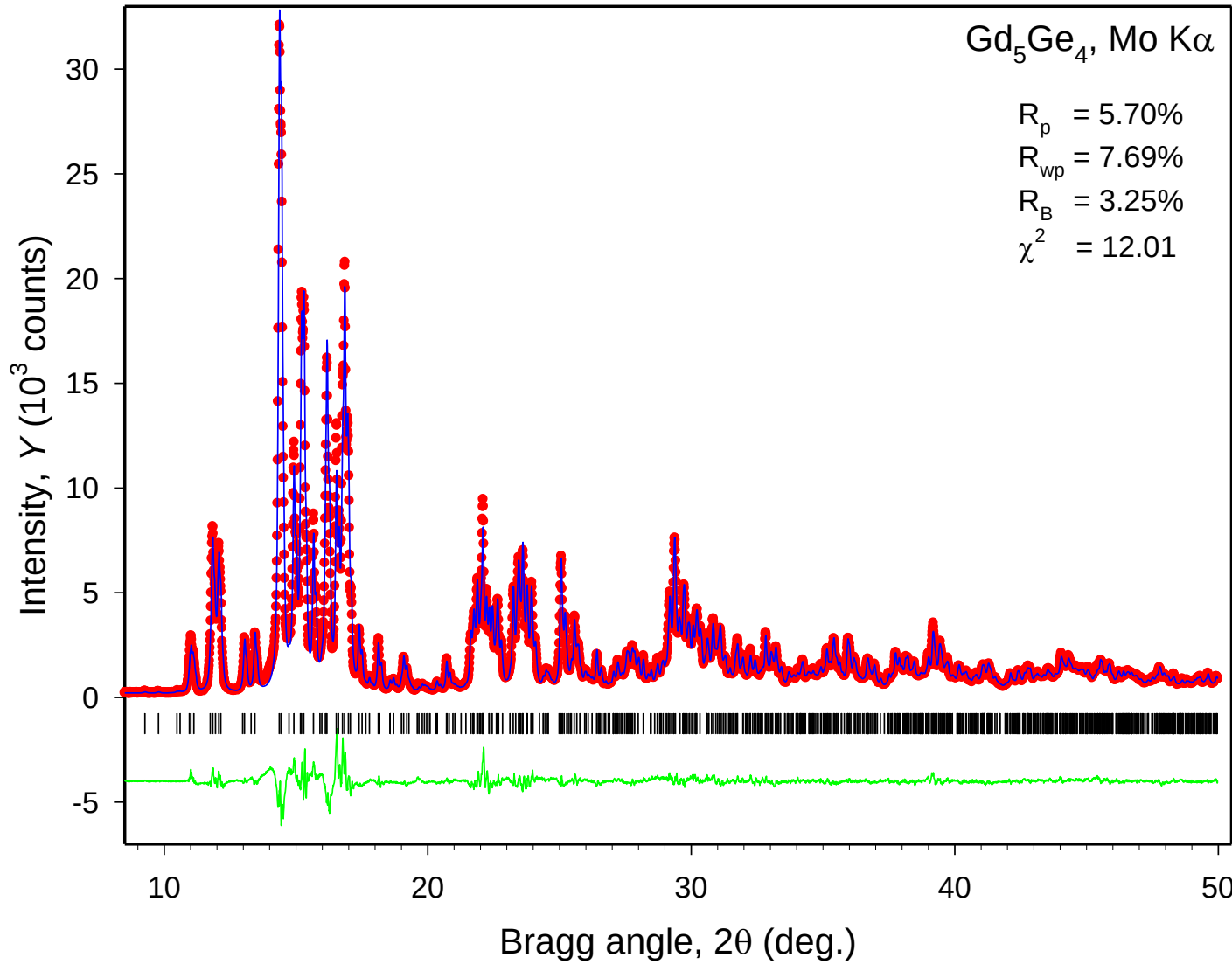
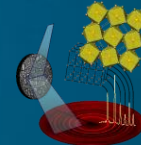


Figure 19.9. The observed and calculated powder diffraction patterns of Gd_5Ge_4 after the completion of Rietveld refinement. A total of 809 independent Bragg reflections are possible in the examined range of Bragg angles

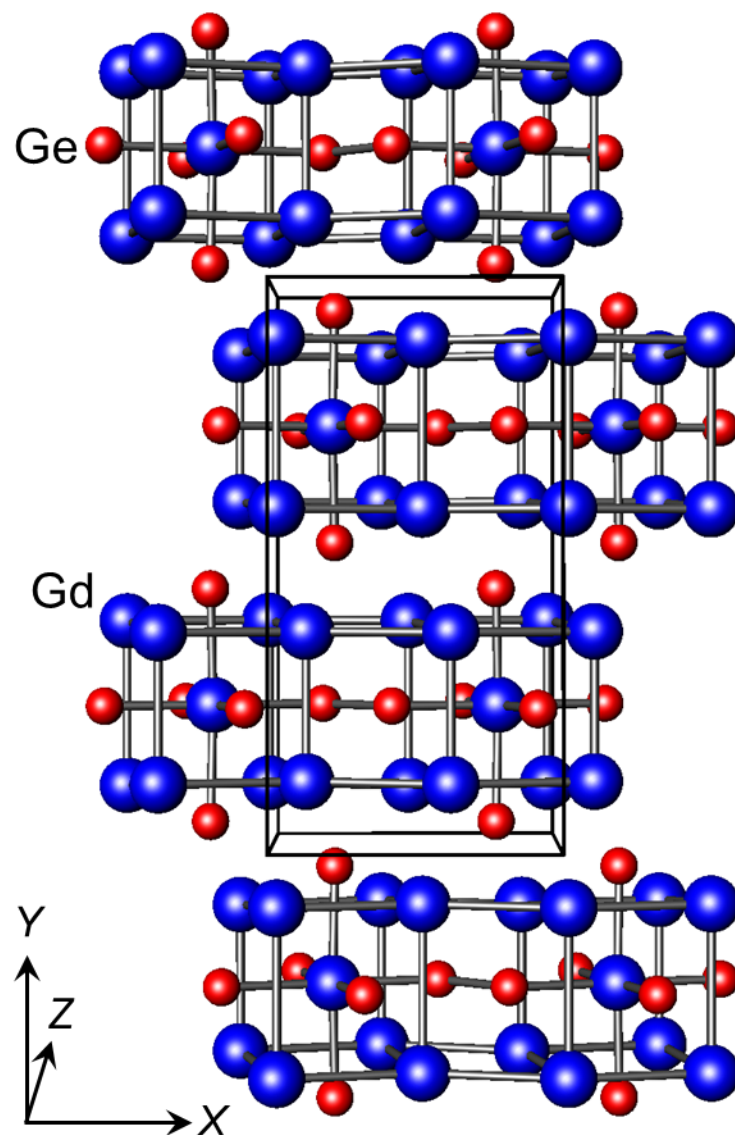
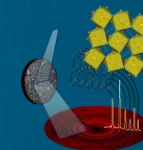


Figure 19.10. The model of the crystal structure of Gd_5Ge_4 as determined by Rietveld refinement. The slabs, which are infinite along X and Z and are limited to $\sim 7 \text{ \AA}$ thickness along Y , are shown as bonded Gd and Ge atoms.

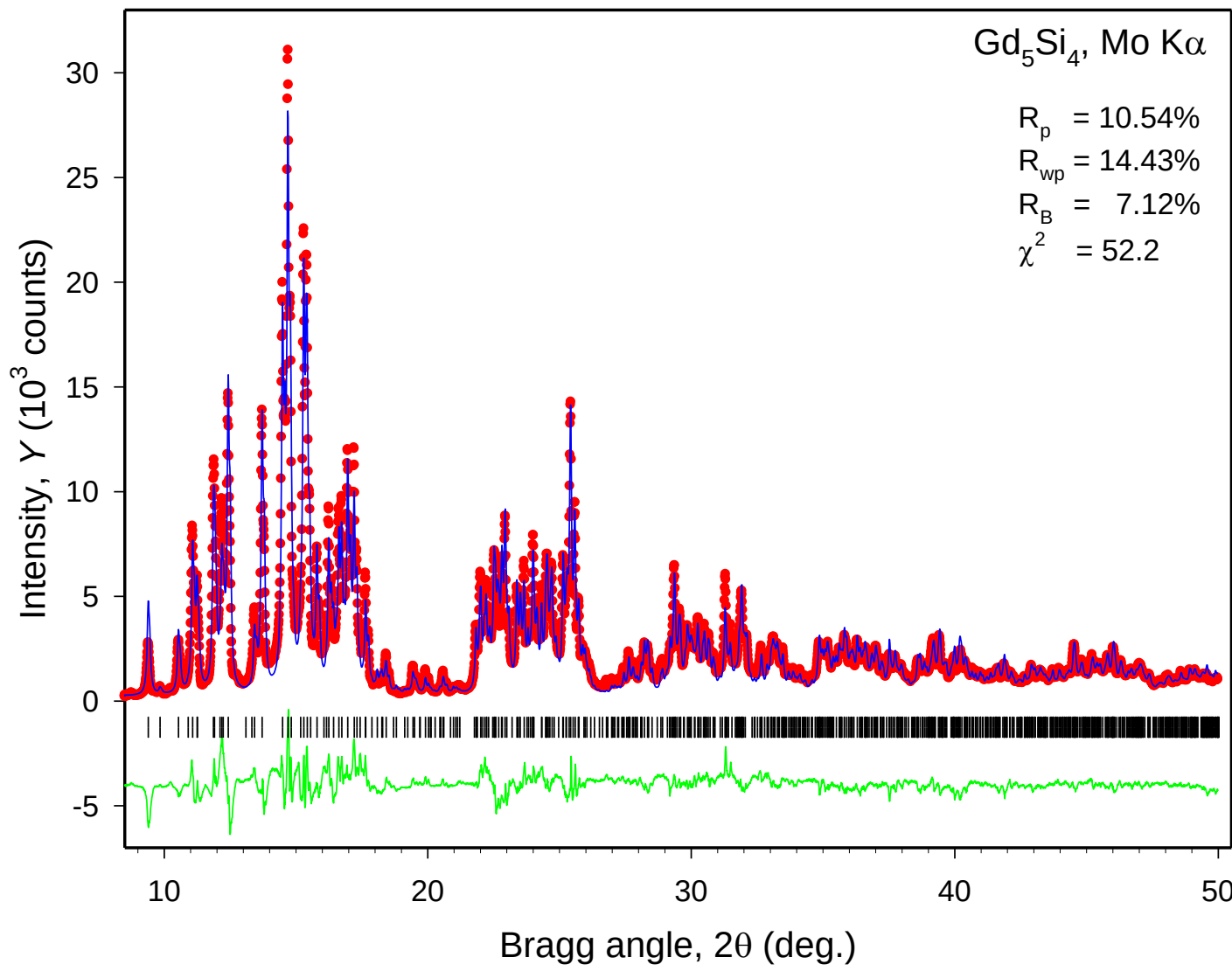
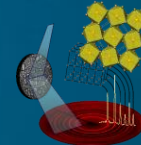


Figure 19.11. The observed and calculated powder diffraction patterns of Gd_5Si_4 after only the coordinates of Gd atoms have been refined together with the phase scale factor. Compare this figure with Figure 19.5.

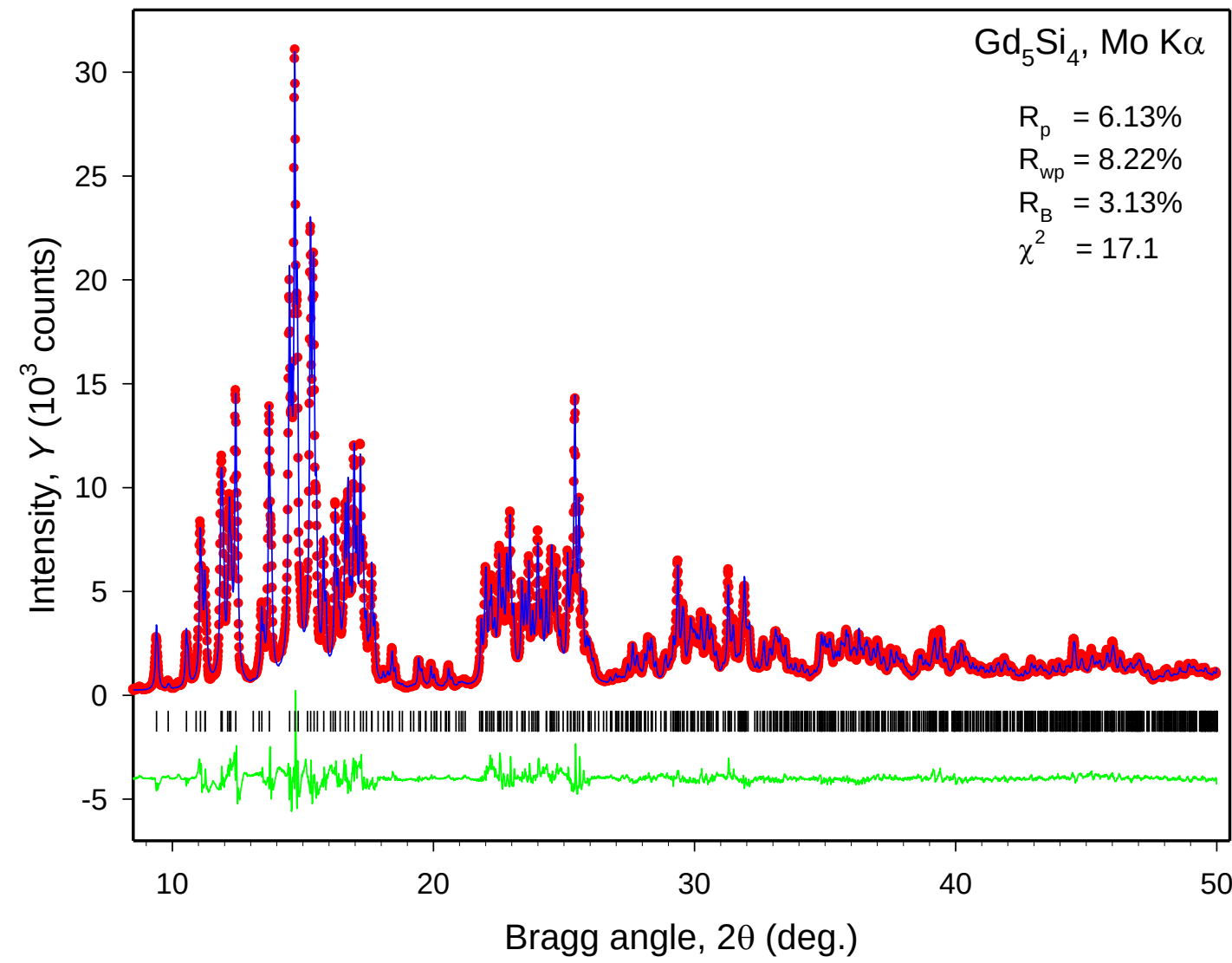
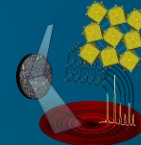


Figure 19.12. The observed and calculated powder diffraction patterns of Gd_5Si_4 after the completion of the refinement using Pearson-VII peak-shape function. A total of 808 independent Bragg reflections are possible in the examined range of Bragg angles.

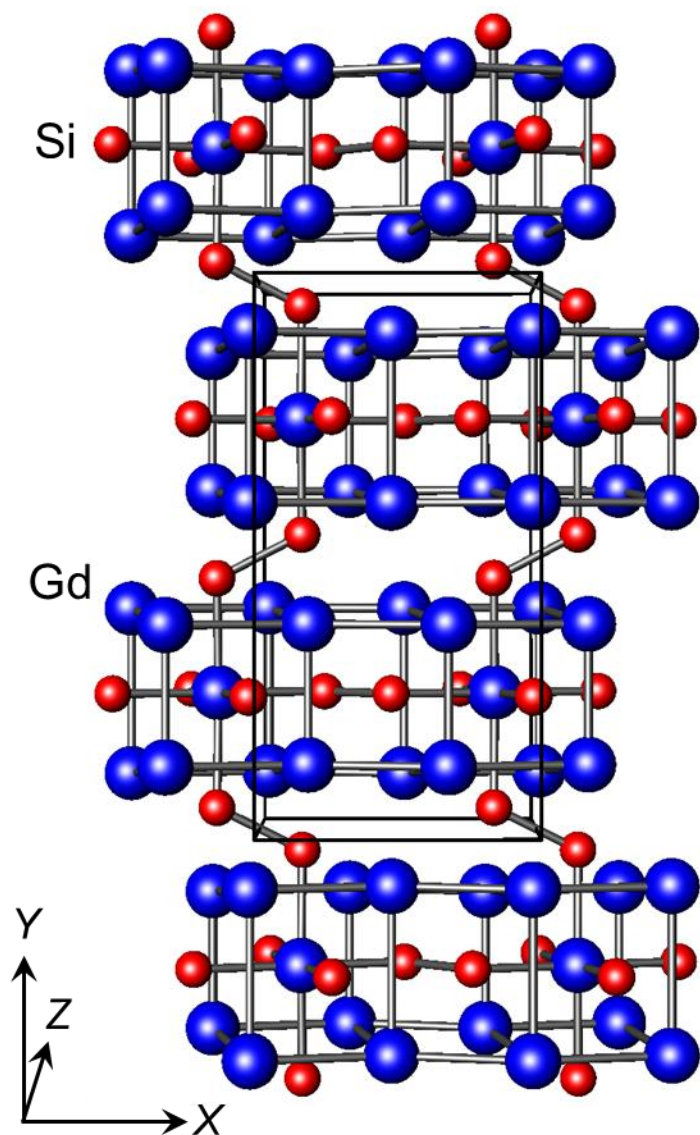
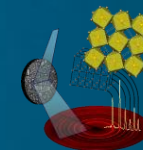


Figure 19.13. The model of the crystal structure of Gd_5Si_4 as determined by Rietveld refinement. The slabs, which are infinite along X and Z and limited along Y to $\sim 7 \text{ \AA}$, are shown as bonded Gd and Si atoms. The major difference between this structure and Gd_5Ge_4 (Figure 19.10) is the presence of short Si-Si interslab bonds (which are connected by gray lines) here, and the absence of short Ge-Ge bonds between the slabs in Gd_5Ge_4 .

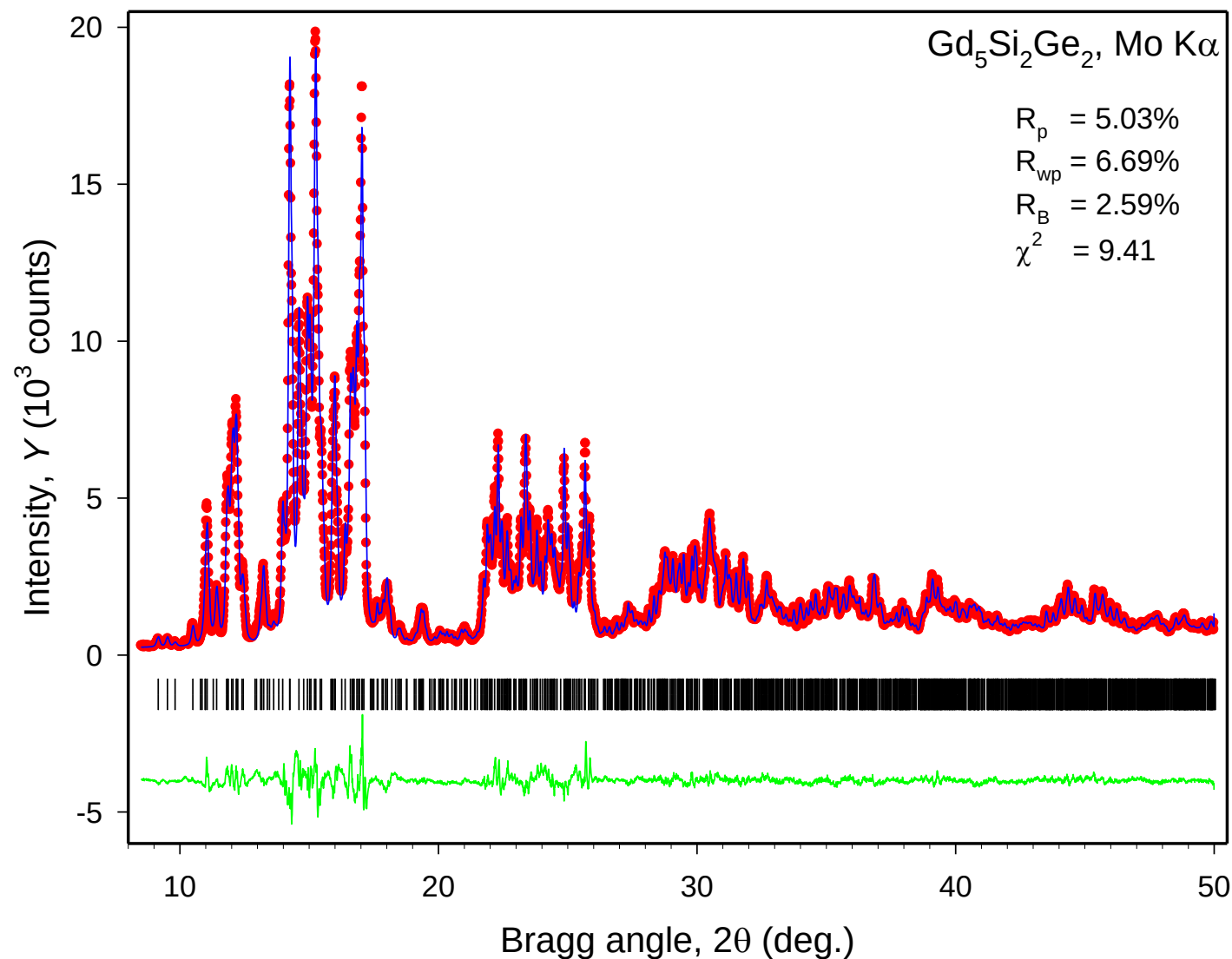
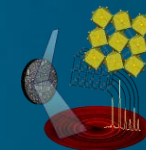


Figure 19.14. The observed and calculated powder diffraction patterns of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ after completion of Rietveld refinement. Compare this figure with Figure 19.8. A total of 1532 independent Bragg reflections are possible in the examined range.

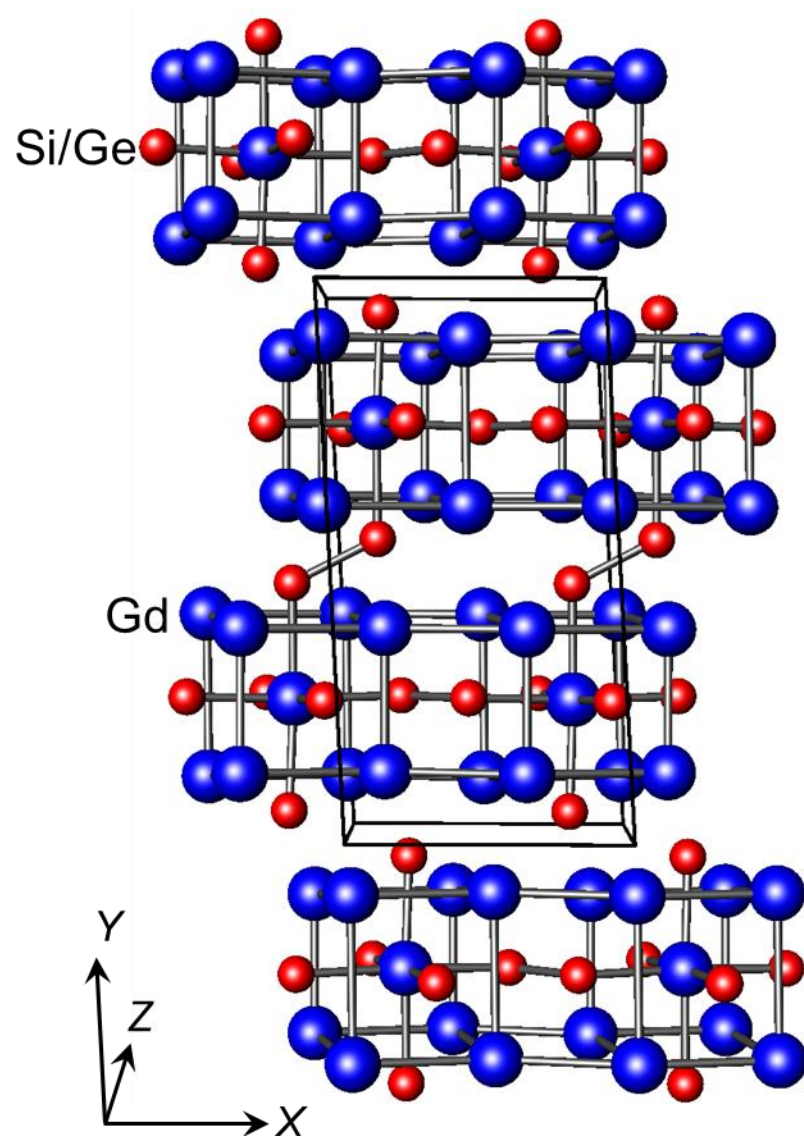
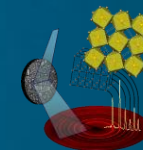


Figure 19.15. The model of the crystal structure of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ as determined by Rietveld refinement. The slabs, which are infinite along X and Z and limited along Z to ~ 7 Å are shown as bonded Gd and Si atoms. This structure is intermediate between Gd_5Ge_4 (Figure 19.10) and Gd_5Si_4 (Figure 19.13): only pairs of slabs (A–B) are connected with short (Si,Ge) – (Si,Ge) bonds, while no such bonds exist between the pairs (A–B and C–D).

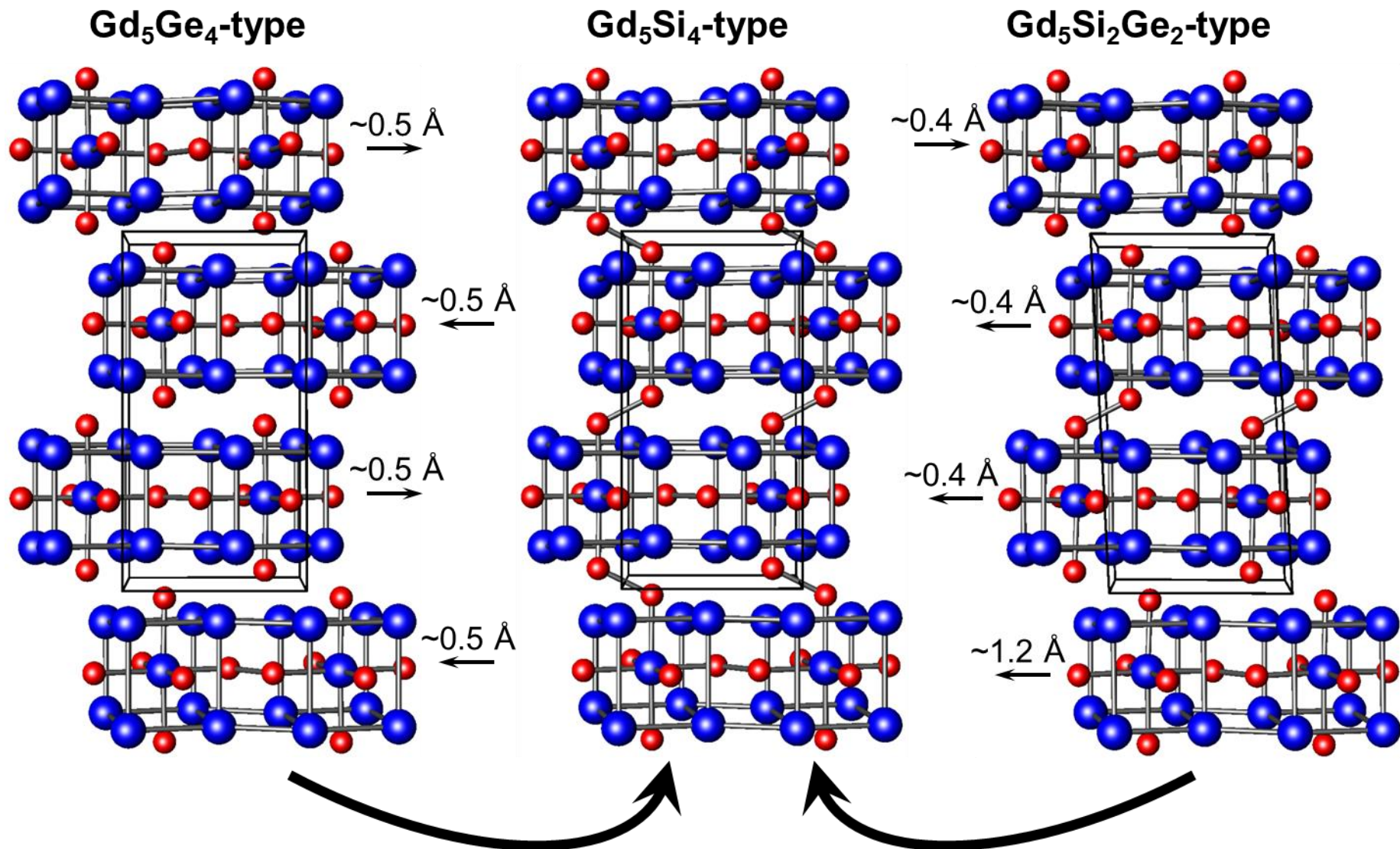
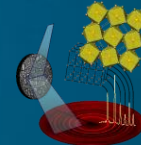


Figure 19.16. The nature of the crystallographic phase changes when the Gd_5Ge_4 -type (*left*) or the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type structures (*right*) transform into the Gd_5Si_4 -type structure.

Short black arrows indicate the directions and the numbers above the arrows the extent of the interslab shear.