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Electron Microscopy Investigation on Empty Germanium Clathrate-II

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The empty clathrate-II of germanium (Fig. 1) is an open, covalently bonded 3D network of tetrahedrally coordinated Ge atoms forming pentagon-dodecahedral Ge_{20} and hexakaidecahedral Ge_{28} cages. Each unit cell contains 16 pentagon dodecahedra and 8 hexakaidecahedra, which provide space for 24 cage positions in a completely filled clathrate. Consequently, the empty clathrate-II is best described by the formula $\square_{24}Ge_{136}$.

Theoretical studies have predicted a relatively high stability of the clathrates-II Na_xSi_{136} and Na_xGe_{136} ($x \to 0$) with respect to the diamond form of Si and Ge [1], and various methods for their synthesis have been suggested. In contrast to Na_xSi_{136} ($x < 1$), which can be synthesized as a mixture with silicon by thermal decomposition of NaSi in dynamic vacuum [2], all attempts to synthesize an empty or almost empty clathrate-II of germanium failed so far. Attempts to prepare guest-free Si and Ge clathrates using *direct* reactions have been unsuccessful in any case.

We could recently report the high-yield synthesis of empty clathrate $\square_{24}Ge_{136}$ through soft oxidation of Ge_9^{4-} Zintl anions [3]. X-ray powder diffraction patterns of the polycrystalline product indicated the presence of a small content of α-Ge. The major phase was completely indexed with the face-centered cubic lattice and a lattice parameter of a = 15.2152(1) Å. Full-profile refinement [4] of the crystal structure from powder diffraction data confirmed the clathrate-II germanium framework (space group $Fd\overline{3}m$). Within the e.s.d. the cationic positions were found to be empty. High-resolution transmission electron microscopy (HRTEM) showed that the product contained one major crystalline phase ($\square_{24}Ge_{136}$) and two minor phases, one being amorphous and one crystalline. The selected-area electron diffraction (SAED) patterns confirmed the cubic symmetry and unit-cell parameters of the clathrate-II structure (Fig. 2). The agreement between experimental and simulated images (Fig. 3) was rather good, thus supporting the results of the X-ray crystal-structure refinement. However, the complete absence of sodium in the cages of the structure cannot doubtlessly be deduced from HRTEM. Only investigations by electron energy-loss spectroscopy (EELS) clearly revealed the absence of Na in the clathrate phase: no Na-*K* edge at 1072 eV was observed in the EEL spectra (Fig. 4). Thus the cages of crystalline $\square_{24}Ge_{136}$ are essentially empty.

References

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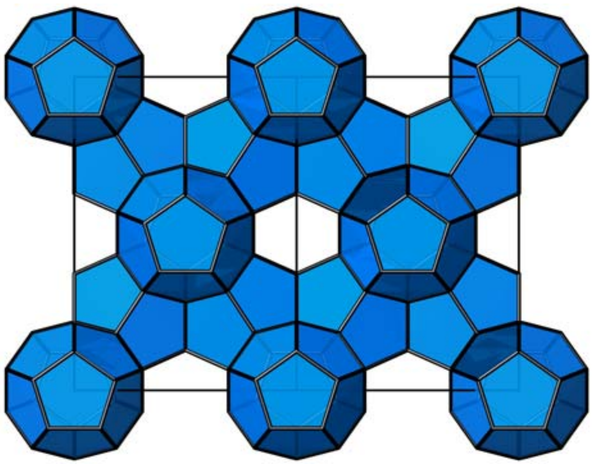


FIG. 1. Unit cell of clathrate-II $\square_{24}Ge_{136}$ viewed along [110]. The crystal structure contains two basic motifs: distorted pentagon dodecahedra (blue) with 20 Ge atoms and hexakaidecahedra (not highlighted) with 28 Ge atoms.

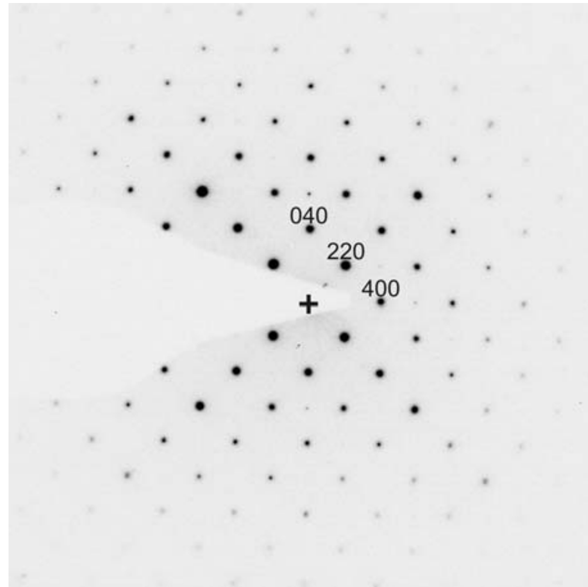
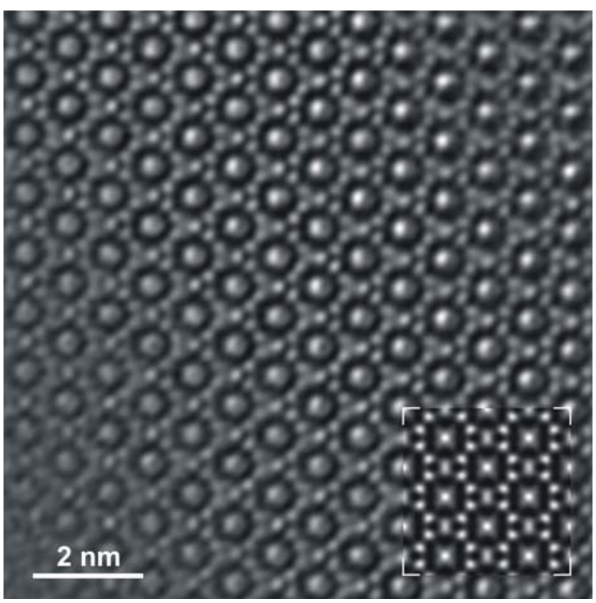


FIG. 2. SAED pattern of clathrate $\square_{24}Ge_{136}$ for the [100] zone axis.



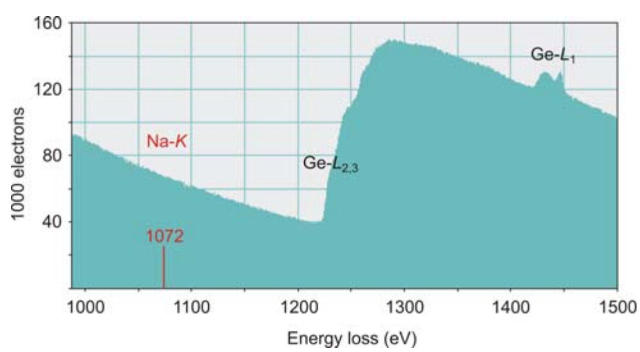


FIG. 4. EEL spectrum of a $\square_{24}Ge_{136}$ micro-crystallite (in [100] orientation) showing $L_{2,3}$ and L_1 edges of germanium at 1217 eV and 1414 eV, respectively. The Na-K edge should appear at 1072 eV.

FIG. 3. HRTEM image of clathrate $\square_{24}Ge_{136}$ taken around SCHERZER optimum focus for zone axis [110]. A simulated image (multi-slice formalism) is inserted; defocus: Δf = -50 nm, specimen thickness: t = 4.3 nm. The Tecnai G2-F30 electron microscope with super-twin lens (C_S = 1.2 mm) was operated at 300 kV (point resolution 0.2 nm).

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