*Supplementary Material*

# New Insights into the Crystal Chemistry of FeB-Type Compounds: The Case of CeGe

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## 1. Crystallographic Data from Powder X-ray Diffraction Data

**Table S1.** Comparison of lattice parameters of CeGe.

| Sample type | *a* / Å | *b* / Å | *c* / Å | Reference | Contained Phases |
|---|---|---|---|---|---|
| Powder | 8.354 | 4.082 | 6.033 | [1] | |
| Powder | 8.337 | 4.061 | 6.045 | [2] | |
| Powder | 8.355 | 4.078 | 6.023 | [3] | |
| Powder | 8.3524(4) | 4.0852(2) | 6.0322(3) | This work, 293 K (Figure S2)) | 82.9% CeGe, 1.7% Ge, 3.0% $CeO_2$, 12.4% $Ce_5Ge_4$ |
| Single crystal | 8.354(4) | 4.073(2) | 6.029(3) | This work, 100 K | CeGe |

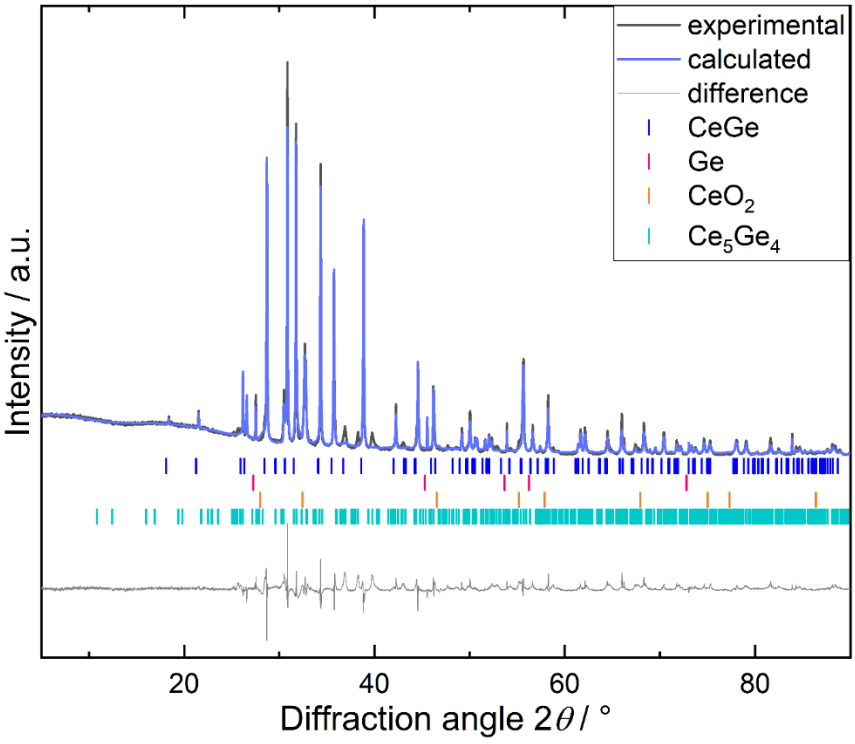


**Figure S1.** Powder diffraction pattern of one obtained sample.2. Crystallographic data from single crystal X-ray diffraction data.

## 2. Crystallographic data from single crystal X-ray diffraction data

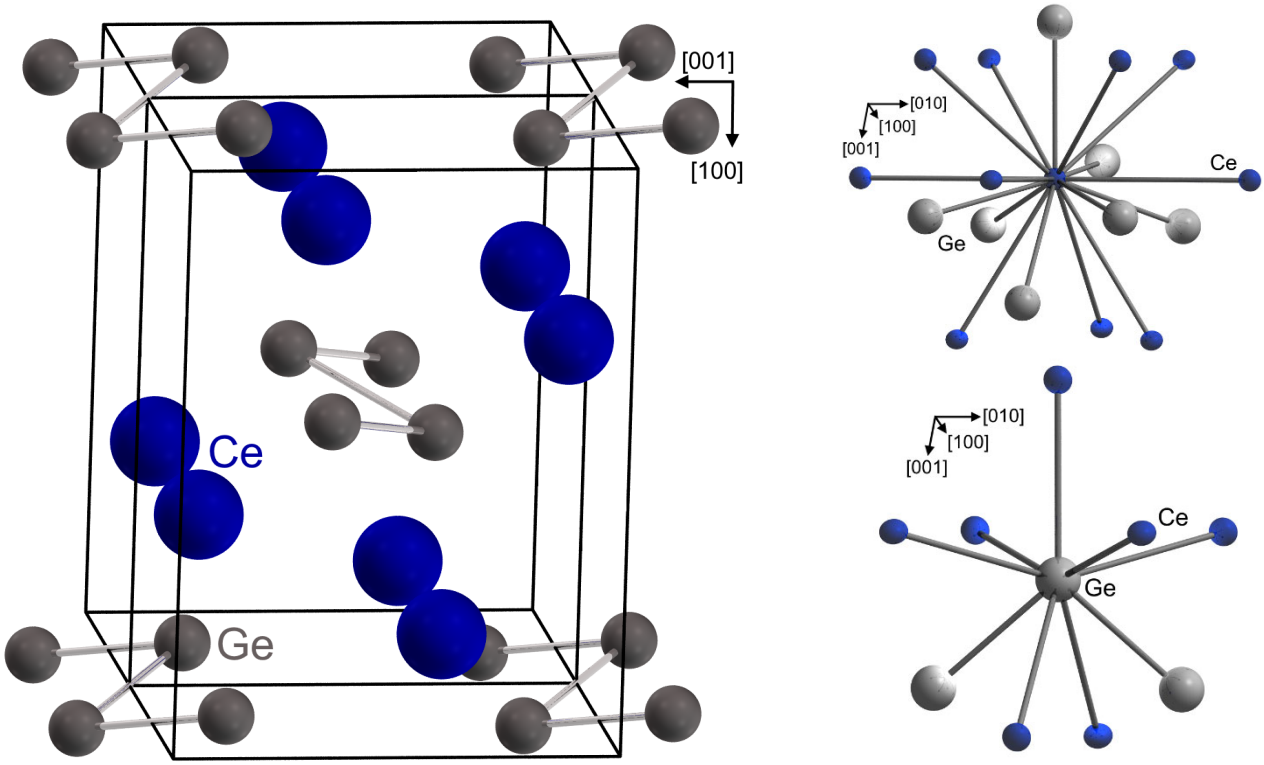


**Figure S2.** Crystal structure of CeGe. (left) Unit cell with Ge-chains running along [010] direction. (right) Coordination environment of Ce and Ge, respectively.

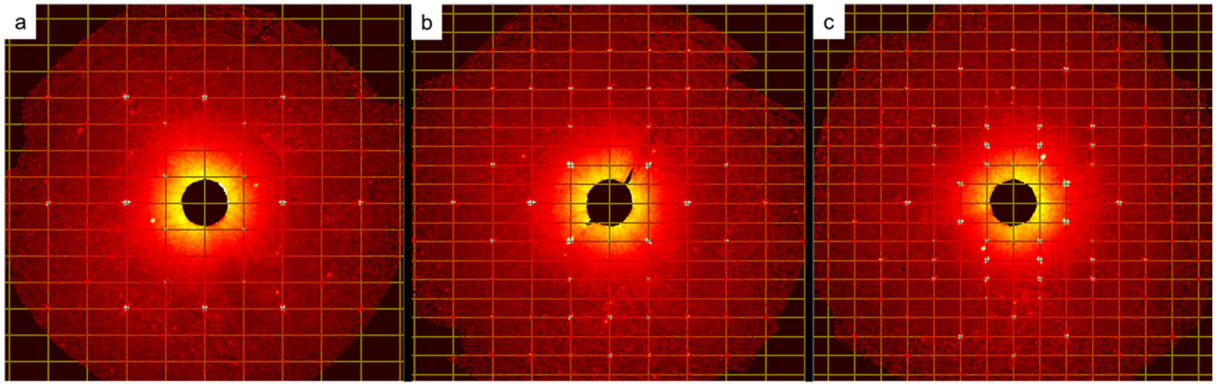


**Figure S3.** Diffraction pattern of CeGe with reciprocal lattice reconstructions of (**a**) (*hk*0), (**b**) (*h*0*l*), and (**c**) (0*kl*) layers.

## 3. Thermal Analysis

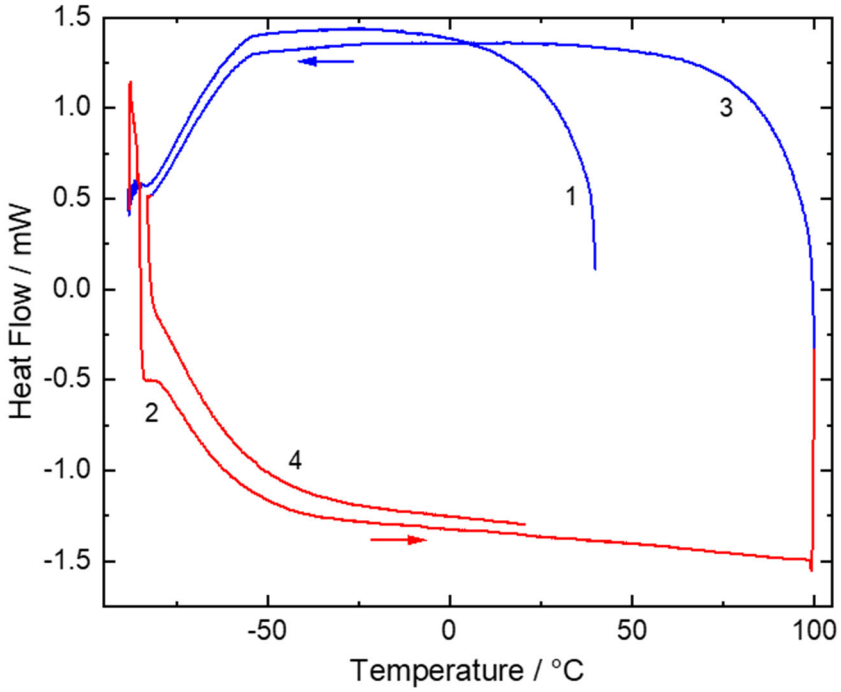


**Figure S4.** DSC, 1,3-first and second cooling, 2,4-first and second heating. Note the absence of any indication of a phase transformation in the interval measured.

### 4. Distances in Ge-polyanionic Motifs

**Table S2.** Binary alkaline earth and rare earth metal germanides comprising Ge-polyanions. Average distances are given for chain motifs.

| Structure Type | Compound | Connectivity | Structural Motif | Distance in Chain | Ref. |
|---|---|---|---|---|---|
| $Ca_7Sn_6$ | $Ca_7Ge_6$ | (1*b*); (1*b*) + (2*b*) | Two layer types: dumbbells; chain fragments | 2.549 | [4] |
| | $Sr_7Ge_6$ | | | 2.569 | [5] |
| | $Ba_7Ge_6$ | | | 2.571 | [5] |
| CrB | CaGe | (2*b*) | infinite trans-trans chains | 2.592 | [6] |
| | SrGe | | | 2.622 | [7] |
| SrSi | | (1*b*)+(2*b*) + (3*b*) | planar $Si_{10}$ units | - | [8] |
| CrB | BaGe | (2*b*) | infinite trans-trans chains | 2.638 | [7] |
| FeB | LaGe | | | 2.667 | [9] |
| LaSi | | (2*b*) | infinite cis-trans- cis-tans chains | 2.621; 2.799 | [10] |
| FeB | CeGe | (2*b*) | infinite trans-trans chains | 2.674 | this work |
| | PrGe | | | 2.649 | [11] |
| CrB | | | | 2.67 | [11] |
| | NdGe | | | 2.711 | [11] |
| | SmGe | | | 2.65 | [12] |
| | EuGe | | | 2.60 | [13] |
| | GdGe | | | 2.632 | [12] |
| | TbGe | | | 2.666 | [14] |
| | DyGe | | | 2.551 | [15] |
| | HoGe | | | 2.639 | [16] |
| | ErGe | | | 2.668 | [11] |
| | TmGe | | | 2.571 | [17] |
| FeB | LuGe | | | 2.597 | [18] |

| | | | | | |
|---|---|---|---|---|---|
| $Ba_3Ge_4$ | $Ba_3Ge_4$ | (2*b*)+(3*b*) | isolated butterflies + trans-trans butterfly-chains | 2.60 | [19] |
| $Er_3Ge_4$ | $Gd_3Ge_4$ | (1*b*) + (2*b*) | chain fragments | 2.632 | [20] |
| $\alpha$-$GdSi_{2-x}$ | $LaGe_{1.6}$ | (3*b*) | network | 2.449 | [21] |
| $TbGe_2$ | $TbGe_2$ | (2*b*)+(3*b*),(4*b*) | two layer types: zig-zag chains + $Si_4$-square nets | 2.446 | [22] |
| $ZrSi_2$(-defect) | $TmGe_2$ | (2*b*),(4*b*) | | 2.544 | [23] |
| | $LuGe_{2(-x)}$ | | | 2.683 | [24] |
| $Y_3Ge_5$ | $Y_3Ge_5$ | (3*b*) | interconnected chains | 2.560 | [25] |
| $Y_3Ge_5$-defect | $Sm_3Ge_5$ | | | 2.556 | [26] |
| | $Gd_3Ge_5$ | | | 2.5625 | [26] |
| | $Tb_3Ge_5$ | | | 2.566 | [27] |
| | $Ho_3Ge_5$ | | | 2.546 | [28] |
| $DyGe_3$ | $YGe_3$ | (2*b*), (5*b*) | two types of layers: Chains + double sheets | 2.72 | [29] |
| $DyGe_3$-defect ("$Y(Ga_{0.13}Ge_{0.87})_{3.34}$") | $PrGe_{3+x}$ | | | 2.544 | [30] |
| | $NdGe_{3+x}$ | | | 2.575 | [30] |
| $DyGe_3$ | $TbGe_3$ | | | 2.547 | [31] |
| | $DyGe_3$ | | | 2.505 | [32] |
| | $HoGe_3$ | | | 2.535 | [33] |
| | $ErGe_3$ | | | 2.579 | [34] |
| | $TmGe_3$ | | | 2.541 | [32] |
| | $LuGe_3$ | | | 2.585 | [35] |

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