

**Na<sub>5</sub>GaGe<sub>2</sub>: A New Intermetallic Compound with an Isolated Linear Anion of GaGe<sub>2</sub><sup>5-</sup>**

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Metalloids, such as germanium, often generate binary compounds with Zintl anions, when combined with electropositive alkali or alkaline earth metals.<sup>1-3</sup> Because of large difference in electronegativity between two components, ionic model suitably represents the transfer of electrons from metal cations to Zintl anions. In order to satisfy closed-shell configuration, Zintl anions tend to form network structure or clusters. Binary or ternary intermetallic compounds of germanium provide ample examples of Zintl anions. A series of different geometries have been observed, such as 3D-networks,<sup>4</sup> 2D-sheets,<sup>5</sup> 1D-strings,<sup>6-8</sup> or isolated clusters in a polyhedral shape.<sup>9,10</sup>

A few mixed group III/IV anions are also known, but no such structural variety in Ge anions have been observed. Known Ga/Ge mixed anions all have 3D-network structures.<sup>11-15</sup> Some contain clathrate units which drew intensive study for possible use as thermoelectric materials.<sup>12-15</sup> Some theoretical studies on Ga/Ge mixed anionic clusters have also been carried out,<sup>16-18</sup> but no compound with such isolated anionic entity has actually been attained. We report a rare example of an isolated Ga/Ge mixed anion, GaGe<sub>2</sub><sup>5-</sup>, with an interesting bonding configuration similar to the one observed in molecular CO<sub>2</sub>.

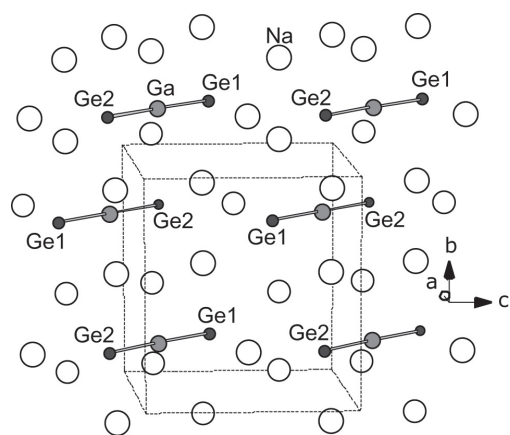
The crystal structure of the new Na-rich intermetallic compound, Na<sub>5</sub>GaGe<sub>2</sub>, is given in Figure 1. Related crystallographic data on Na<sub>5</sub>GaGe<sub>2</sub> are provided in Table 1-3. An isolated anion of GaGe<sub>2</sub><sup>5-</sup> has linear conformation and is separated from others by surrounding cations of Na<sup>+</sup>. Those linear anions are all aligned

ed along (1,0,-1) direction, and placed in alternating manner. Two Ge bound to central Ga in the ∠ Ge-Ga-Ge bond angle of 177.4° (near 180°). Two Ge-Ga bonds have near identical bond lengths of 2.343 and 2.354 Å. The lengths of these bonds are much shorter than any known or theoretically calculated Ge-Ga bonds. The Ge-Ga bond lengths in LiGaGe and Ce<sub>3</sub>Ga<sub>9</sub>Ge, which

**Table 1.** Crystallographic data for Na<sub>5</sub>GaGe<sub>2</sub>

Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>m</i>
Unit cell dimensions	<i>a</i> = 5.6218(6) Å <i>b</i> = 9.270(1) Å <i>c</i> = 8.2617(9) Å <i>β</i> = 97.981(3)°
Volume (Å <sup>3</sup> )	426.40(8)
<i>Z</i>	2
Density (calcd/ mg m <sup>-3</sup> )	2.569
Absorption coefficient (mm <sup>-1</sup> )	10.291
Temperature (K)	173(2)
F(000)	300
Crystal size (mm <sup>3</sup> )	0.15 × 0.12 × 0.10
θ range for data collection (°)	2.49 to 30.49
Index ranges	-7 ≤ <i>h</i> ≤ 8, -13 ≤ <i>k</i> ≤ 13, -11 ≤ <i>l</i> ≤ 11
Reflections collected	5039
Independent reflections	1369 [R(int) = 0.0369]
Data / restraints / parameters	1369 / 0 / 43
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.048
Final R indices [I > 2σ(I)] <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.0306, <i>wR</i> <sub>2</sub> = 0.0654
R indices (all data) <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.0429, <i>wR</i> <sub>2</sub> = 0.0712
Largest diff. peak and hole (e. Å <sup>-3</sup> )	0.834 and -0.840

<sup>a</sup>*R*<sub>1</sub> = Σ||*F*<sub>o</sub>l - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>l. *wR*<sub>2</sub> = [Σ*w*(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>/Σ(*wF*<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>, where *w* = 1/σ(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup> + (*gP*)<sup>2</sup> + *jP*, *P* = [max(*F*<sub>o</sub><sup>2</sup>, 0) + 2*F*<sub>c</sub><sup>2</sup>]/3. *g* = 0.033, *j* = 0.0.



**Figure 1.** Crystal structure of Na<sub>5</sub>GaGe<sub>2</sub>. Large open circles are Na<sup>+</sup>. Isolated anions of GaGe<sub>2</sub><sup>5-</sup> all aligned along same direction, and are placed in alternating manner, as indicated by positions of Ge1 and Ge2.

**Table 2.** Atomic coordinates (× 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) for Na<sub>5</sub>GaGe<sub>2</sub>

	Wyckoff	x	y	z	U(eq)
Ge(1)	2e	5397(1)	2500	3544(1)	11(1)
Ge(2)	2e	672(1)	2500	8389(1)	13(1)
Ga(1)	2e	3107(1)	2500	932(1)	11(1)
Na(1)	4f	4057(3)	5774(2)	3107(2)	31(1)
Na(2)	4f	8201(3)	726(2)	1159(2)	21(1)
Na(3)	2e	659(4)	2500	4823(2)	30(1)

U(eq) is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

**Table 3.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Na}_5\text{GaGe}_2$ 

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Ge(1)	10(1)	14(1)	10(1)	0	2(1)	0
Ge(2)	15(1)	14(1)	11(1)	0	0(1)	0
Ga(1)	9(1)	13(1)	12(1)	0	1(1)	0
Na(1)	37(1)	23(1)	29(1)	-10(1)	-7(1)	12(1)
Na(2)	22(1)	18(1)	26(1)	-2(1)	12(1)	1(1)
Na(3)	11(1)	65(2)	16(1)	0	4(1)	0

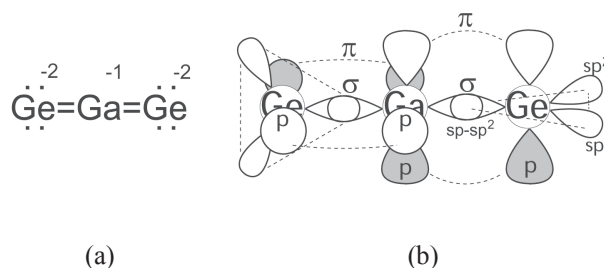
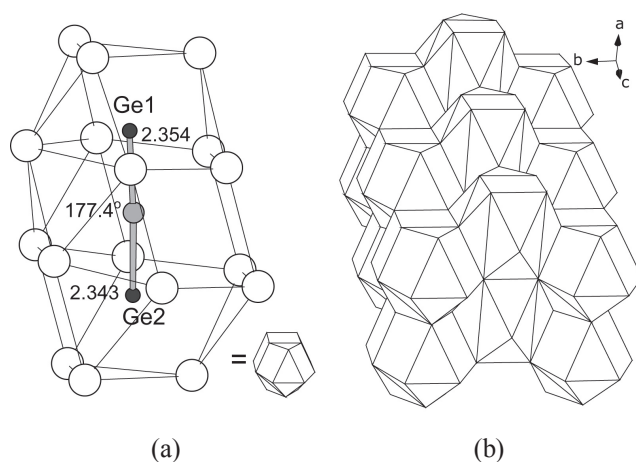
The anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^*U_{11} + \dots + 2hka^*b^*U_{12}]$ .

are known ternary compounds with 3D-network structure, are 2.582 (average) and 2.594  $\text{\AA}$ .<sup>11,19</sup> Ge-Ga bond lengths in a hypothetical rectangular cluster of  $\text{Ga}_2\text{Ge}_2$  are calculated to be 2.430 - 2.485  $\text{\AA}$ .<sup>17</sup> Ge-Ga bond lengths in a hypothetical cluster compound of  $\text{NaGaGe}_3$  ( $\text{GaGe}_3^{1-}$  anionic cluster) are calculated to be 2.590 - 3.991  $\text{\AA}$ .<sup>16</sup> Theoretical ab initio calculation indicated the involvement of aromaticity by delocalization of  $\pi$ -electrons in those hypothetical cluster compounds.<sup>16-18</sup> Therefore, the extent of relative shortening of Ge-Ga bonds in  $\text{Na}_5\text{GaGe}_2$  is substantial, which strongly indicates multiple bonding characteristics.

The isolated anion of  $\text{GaGe}_2^{5-}$  provides an interesting example of an application of valence bonding model to a simple cluster. Large difference of electronegativity among constituent elements predicts near complete charge transfer (ionic model) from highly electropositive Na to remainders. The bonding between Ga and Ge is highly covalent, and the isolated anion of  $\text{GaGe}_2^{5-}$  is considered to have closed-shell electron configuration. Figure 2a shows postulated Lewis structure of  $\text{GaGe}_2^{5-}$ . Having 16 valence electrons, the structure has same conformation as that of  $\text{CO}_2$ . The Lewis structure corroborates the significantly short Ge-Ga bond lengths and near linear conformation observed above. Bonding configuration of the double bonds can be deduced by application of valence bonding model. The postulated bonding configuration based on the model is schematically represented in Figure 2b. Explanation of bonding configuration of  $\text{GaGe}_2^{5-}$  via valence bonding model follows the same pattern as the one applied to  $\text{CO}_2$ . Major difference is that 4s and 4p electrons participate in the bonding interaction of  $\text{GaGe}_2^{5-}$ , whereas they were 2s and 2p electrons in  $\text{CO}_2$ .

The  $\text{GaGe}_2^{5-}$  anion is surrounded by  $17 \times \text{Na}^+$ , which arrange into a cocoon-shaped cage, shown in Figure 3a. Coordination spheres around two Ge are non-identical. Ge2 is coordinated to  $9 \times \text{Na}^+$ , whereas Ge1 to  $8 \times \text{Na}^+$ . This subtle difference in coordination spheres around two Ge is suggested to cause the minor deviation observed in  $\text{GaGe}_2^{5-}$ , from symmetric linear structure predicted by valence bonding model. Space-filling packing of the cages is shown in Figure 3b. Non-symmetric shape of the cage necessitates packing in alternating manner. Thereby, linear anions are also aligned in alternating manner, as can be seen in Figure 1a.

$\text{Na}_5\text{GaGe}_2$  provides the first and rare example of Ga/Ge mixed anion obtained as an isolated entity in Na-rich composition. In previously known intermetallic compounds, such as  $\text{LiGaGe}$ ,  $\text{A}_8\text{Ga}_{16}\text{Ge}_{30}$  ( $\text{A}=\text{Sr}, \text{Eu}$ ),  $\text{Cs}_8\text{Ga}_8\text{Ge}_{38}$ , or  $\text{EuGa}_2\text{Ge}_4$ , relatively

**Figure 2.** (a) Lewis structure, and (b) postulated bonding configuration of the isolated linear anion of  $\text{GaGe}_2^{5-}$ .**Figure 3.** (a) Coordination spheres around Ga and Ge. Large open circles are Na. The linear anion of  $\text{GaGe}_2^{5-}$  resides in the cocoon-shaped cage generated by  $17 \times \text{Na}^+$ , which corresponds to a basic building unit as combined. (b) Crystal structure of  $\text{Na}_5\text{GaGe}_2$  can be represented as packing of the building units in alternating manner.

small numbers of alkali or alkaline earth cations were nesting in Ga/Ge mixed anion in a 3D-network structure.<sup>11-15</sup> On the contrary,  $\text{GaGe}_2^{5-}$  in  $\text{Na}_5\text{GaGe}_2$  was obtained as an isolated entity embedded in relatively larger number of alkali metal cations. As the composition became rich in Na, propensity to decompose apparently increased, that may explain why such compound has not been obtained. Upon exposure to air, the crystals of  $\text{Na}_5\text{GaGe}_2$  immediately decomposed into black powder. Even in poly(butene) oil, inert gas had to be used in order to stop the facile decomposition. In view of the relative size of the isolated anionic entity,  $\text{GaGe}_2^{5-}$  resides at the end of the smallest possible one attainable for Ga/Ge mixed composition. One hypothetical entity presumed to be smaller than  $\text{GaGe}_2^{5-}$ , which is still remaining to be found, is  $\text{GaGe}^{3-}$ . From this report of obtaining  $\text{GaGe}_2^{5-}$  as an isolated anion, it became quite plausible that those hypothetical small anionic clusters, such as  $\text{GaGe}^{3-}$  or  $\text{GaGe}_3^{1-}$ , might be obtainable as a real compound in an alkali metal-rich composition, if care was taken to eliminate decomposition of the product.

## Experimental

$\text{Na}_5\text{GaGe}_2$  was synthesized as single crystals from constituent elements in molten Na, as described in previous reports on

syntheses of mixed metal nitrides.<sup>20-22</sup> Reactants used for the synthesis were  $\text{NaN}_3$  (109.2 mg, Aldrich, 99%), Na (254 mg, Aldrich, 99%), Sr (44.0 mg, Aldrich, +99%), Ge (72.5 mg, Cerac, 99.999%), Ga (70.2 mg, Cerac, 99.999%), and Li (3.9 mg, Aldrich, 99.9%). The molar ratio of Na: Sr: Ge: Ga: Li was 13:1/2: 1:1:1/2. Product was obtained as black powder, which readily decomposed when it was exposed in air. Poly(butene) oil was used to prevent decomposition in air during X-ray diffraction data collection. X-ray diffraction data were collected with a Bruker X8 APEX II diffractometer equipped with 4K CCD detector. Initial orientation matrix was obtained by using APEX2 program.<sup>23</sup> The integration of the diffraction data was carried out by the program SAINT.<sup>24</sup> An empirical absorption correction was applied using SADABS.<sup>25</sup> The initial input file for solving the crystal structure was prepared by XPREP.<sup>26</sup> The structure was solved by the direct method, using SHELXS.<sup>27</sup> Refinement of the structure was carried out by the full-matrix least square method (on  $F^2$ ), using SHELXL.<sup>27</sup> The atomic parameters were standardized by using STRUCTURE TIDY.<sup>28</sup> The space group was verified by using ADDSYM.<sup>29</sup> Madelung potential was calculated by EUTAX.<sup>30</sup> The bond valence was not calculated, because the bond-valence parameter for Ga-Ge bond was not available.<sup>31</sup> WDX (wavelength dispersive X-ray) and semi-quantitative (without standard) EDX (energy dispersive X-ray) analyses were carried out by using a JEOL JXA-8900R WD/ED combined microanalyzer.

Under microscope, the product was observed as a mixture of two differently shaped crystals, chunks and needles. Silvery metallic colored chunks with well-defined facets readily decomposed even in poly(butene) oil, that crystallographic analysis on them could not be carried out. Silvery needles tend to coalesce into rectangular column which easily breaks into needles upon being pressed. Indexing on the single crystal diffraction peaks obtained from a rectangular crystal indicated the crystal is a new compound, which belongs to monoclinic system, with unit-cell parameters of  $a = 5.6218(6)$ ,  $b = 9.270(1)$ ,  $c = 8.2617(9)$  Å, and  $\beta = 97.981(3)^\circ$ . EDS semi-quantitative analyses were carried out on several needles in order to obtain the elemental ratio. Only peaks for Ge, Ga and Na were observed with no other ones related to Li or Sr. The atomic ratio of Na/Ga and Ge/Ga were measured to be  $5.5 (\pm 0.2)$  and  $1.82 (\pm 0.02)$ , respectively. Therefore, elemental ratio of Na:Ga:Ge was 5:1:2.

Systematic extinctions in the diffraction data suggested the space group of  $P2_1/m$ . Initial structure solution was obtained by the direct method. Three crystallographic sites with substantial electron densities could immediately be allocated for Ge1, Ge2, and Ga. By including Na1, Na2, and Na3 into the solution, structural refinement reached the level of  $R_I = 3.06\%$ . The atomic ratio between Na, Ga, and Ge was 5:1:2, which conforms to the value obtained by EDS analyses. The empirical formula came out to be  $\text{Na}_5\text{GaGe}_2$ .

**Supplementary Material.** Supplementary material has been

sent to Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (crysdata@fiz-karlsruhe.de, [http://www.fiz-karlsruhe.de/request\\_for\\_deposited\\_data.html](http://www.fiz-karlsruhe.de/request_for_deposited_data.html)), as CSD No. 421450, and can be obtained by contacting the FIZ and quoting the article details and the corresponding CSD number.

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## References

- Schäfer, H. *J. Solid State Chem.* **1985**, *57*, 97.
- Nesper, R. *Prog. Solid State Chem.* **1990**, *20*, 1.
- Nesper, R. *Angew. chem. Int. Ed. Engl.* **1991**, *30*, 789.
- Menges, E.; Hopf, V.; Schäfer, H. *Z. Naturforsch.* **1969**, *24b*, 1351.
- Wallbaum, H. *J. Naturwissenschaften* **1944**, *32*, 76.
- Betz, A.; Schäfer, H.; Weiss, A. *Z. Naturforsch.* **1967**, *22b*, 103.
- Müller, W.; Schäfer, H.; Weiss, A. *Z. Naturforsch.* **1971**, *26b*, 534.
- Park, D. G.; Dong, Y.; DiSalvo, F. J. *J. Alloys and Compounds* **2009**, *470*, 90.
- Betz, A.; Schäfer, H.; Weiss, A. *Z. Naturforsch.* **1967**, *22b*, 103.
- Merlo, F.; Fornasini, M. L. *Acta Cryst.* **1967**, *22*, 919.
- Bockelmann, V. W.; Schuster, H.-U. *Z. Anorg. Allg. Chem.* **1974**, *410*, 233.
- Chakoumakos, B. C.; Sales, B. C.; Mandrus, D. G.; Nolas, G. S. *Journal of Alloys and Compounds* **2000**, *296*, 80.
- Chakoumakos, B. C.; Sales, B. C.; Mandrus, D. G. *Journal of Alloys and Compounds* **2001**, *322*, 127.
- Kröner, R.; Peters, K.; Schnering, H. G. *Zeitschrift fuer Kristallographie-New Crystal Structures* **1998**, *213(4)*, 671.
- Carillo-Cabrera, W.; Paschen, S.; Grin, Y. *Journal of Alloys and Compounds* **2002**, *333*, 4.
- Chi, X. X.; Li, X. H.; Chen, X. J.; Yuang, Z. S. *Journal of Molecular Structure: Theochem* **2004**, *677*, 21.
- Chi, X. X.; Chen, X. J.; Yuan, Z. S. *Journal of Molecular Structure: Theochem.* **2005**, *732*, 149.
- Zhu, X. *Spectrochimica Acta A* **2007**, *66*, 512.
- Zhuravleva, M. A.; Kanatzidis, M. G. *Journal of Solid State Chemistry* **2003**, *173*, 280.
- Park, D. G.; DiSalvo, F. J. *Bull. Korean Chem. Soc.* **2009**, *30(6)*, 1379.
- Park, D. G.; DiSalvo, F. J. *Bull. Korean Chem. Soc.* **2008**, *29(12)*, 2413.
- Park, D. G.; Dong, Y.; DiSalvo, F. J. *Solid State Sciences* **2008**, *10*, 1846.
- Bruker, APEX2 (version 2.10): Software for the CCD system, Bruker Analytical X-ray System, Madison, WI, 2007.
- Bruker, SAINT Plus: Software for the CCD system, Bruker Analytical X-ray System, Madison, WI, 2003.
- Sheldrick, G. M. SADABS; Institute für Anorganische Chemie der Universität Göttingen: Göttingen, Germany, 1999.
- Bruker, XPREP (version 6.14): Software for the CCD system, Bruker Analytical X-ray System, Madison, WI, 2003.
- Sheldrick, G. M. SHELXL 97; Institute für Anorganische Chemie der Universität Göttingen: Göttingen, Germany, 1997.
- Gelato, L. M.; Parthé, E. *J. Appl. Cryst.* **1987**, *20*, 139.
- Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837.
- Ewald, P. P. *Ann. Phys.* **1921**, *64*, 253.
- O'Keeffe, M.; Brese, N. E. *Acta Cryst.* **1992**, *B48*, 152.