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**[Ge<sub>2</sub>]<sup>4-</sup> Dumbbells with Very Short Ge-Ge Distances in the Zintl Phase Li<sub>3</sub>NaGe<sub>2</sub> – a Solid State Equivalent to Molecular O<sub>2</sub>**

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**Abstract:** The novel ternary Zintl phase Li<sub>3</sub>NaGe<sub>2</sub> comprises alkali metal cations and [Ge<sub>2</sub>]<sup>4-</sup> dumbbells. The diatomic [Ge<sub>2</sub>]<sup>4-</sup> unit is characterized by the shortest Ge-Ge distance of 2.390(1) Å observed in a Zintl phase and thus represents the first double bond as also suggested by the (8–N) rule. Raman measurements support these findings. The multiple bond character is confirmed by electronic structure calculations, and an upfield <sup>6</sup>Li NMR shift of –10.0 ppm assigned to those Li cations surrounded by the  $\pi$  systems of three Ge dumbbells further underlines this interpretation. For the unperturbed, ligand-free dumbbell in Li<sub>3</sub>NaGe<sub>2</sub> the  $\pi$ -bonding  $p_y$  and  $p_z$  orbitals are degenerate as in molecular oxygen having singly occupied orbitals. The partially filled  $\pi$ -type bands of the neat solid Li<sub>3</sub>NaGe<sub>2</sub> cross the Fermi level, resulting in metallicity. Li<sub>3</sub>NaGe<sub>2</sub> was synthesized from the elements as well as from binary reactants and subsequently characterized crystallographically.

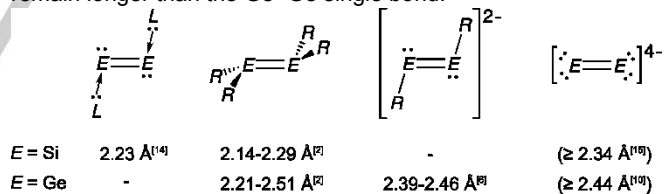
Multiple bonds of the heavier homologues of boron, carbon and nitrogen have been intensively investigated during the last decades.<sup>[1–3]</sup> Among those, the heavier tetrel homologues *E* all adopt a *trans*-bent structure in contrast to planar ethylene. The pyramidalization at the *E* atom in *R*<sub>2</sub>*E*=*ER*<sub>2</sub> drastically influences the possibility of forming a classical  $\pi$ -bond between the two metal atoms for *E* = Ge, Sn, and Pb.

The CGMT model proposed by Trinquier and Malrieu<sup>[4]</sup> traces the deviation from planarity of *R*<sub>2</sub>*E*=*ER*<sub>2</sub> molecules back to the relative values of singlet and triplet energies of the monomeric units *ER*<sub>2</sub> (*E*<sub>S</sub> and *E*<sub>T</sub>, respectively) and the energy of the double bonded system: for *E* <sub>$\sigma^*\pi$</sub>  > 2Δ*E*<sub>S-T</sub> a classical planar structure is obtained, whereas *E* <sub>$\sigma^*\pi$</sub>  < 2Δ*E*<sub>S-T</sub> favors the *trans*-bent structure. *E* <sub>$\sigma^*\pi$</sub>  < Δ*E*<sub>S-T</sub> results in monomeric *ER*<sub>2</sub> fragments without *E*–*E* bonding.<sup>[1,5]</sup> The interatomic *E*–*E* distance is another strong indicator for the bond order. Scheme 1 gives an overview of several homonuclear, double bonded Si and Ge species. For the second row elements, distances of double bonded atoms are considerably shorter than the sum of the covalent radii, whereas for the heavier homologues

deviations occur due to the strict requirements of the often bulky ligands used to stabilize the reactive bonds or due to electrostatic repulsion in case of charged systems. For example, *R*<sub>2</sub>Ge=*GeR*<sub>2</sub> bond lengths are in the range of 2.21 to 2.51 Å,<sup>[2]</sup> most of them being shorter than the Ge-Ge single bond length of 2.44 Å, but in [*R*Ge=*GeR*]<sup>2-</sup> longer distances are observed.<sup>[6]</sup>

In general, *trans*-bent structures are energetically favored over planar structures. Ligand-free and thus symmetrically unperturbed germanide dumbbells have been observed in Zintl phases.<sup>[7]</sup> Assuming a complete valence electron transfer in BaMg<sub>2</sub>Ge<sub>2</sub> results in a 14 valence electron [Ge–Ge]<sup>6-</sup> dumbbell. The bond length of 2.58 Å<sup>[8]</sup> is however significantly longer than the Ge single bond length and sketchily explained by Coulombic repulsion of the negatively charged atoms. Recently, the strong interaction of alkali earth metal (*Ae*) *d* states with anions in Zintl phases was experimentally established, hinting at a less effective electron transfer in case of *Ae* counter ions.<sup>[9]</sup>

Ge dumbbells occur also in binary lithium germanides Li<sub>*x*</sub>Ge<sub>1–*x*</sub> (0.692 ≤ *x* ≤ 0.778).<sup>[10–13]</sup> However, according to the formal electron transfer of the Zintl Klemm concept they never contain a truly double bonded dumbbell [Ge=Ge]<sup>4-</sup>. Either a more highly charged species such as (Li<sup>+</sup>)<sub>13</sub>(Ge<sup>4-</sup>)<sub>2</sub>[Ge<sub>2</sub>]<sup>5-</sup> for Li<sub>13</sub>Ge<sub>4</sub> and (Li<sup>+</sup>)<sub>9</sub>([Ge<sub>2</sub>]<sup>4.5-</sup>)<sub>2</sub> for Li<sub>9</sub>Ge<sub>4</sub> or [Ge<sub>2</sub>]<sup>4-</sup> units with one or 0.5 excess electrons per dimer, respectively, have been considered. Yet, with decreasing Li content  $\pi$ -bonding contributions are expected to increase, and appropriately the Ge–Ge bond lengths decrease from 2.62 Å (Li<sub>13</sub>Ge<sub>4</sub>)<sup>[12,13]</sup> to 2.44 Å (Li<sub>9</sub>Ge<sub>4</sub>)<sup>[10]</sup> but in all cases remain longer than the Ge–Ge single bond.



**Scheme 1.** Types of double bonded heavier tetrel systems and their respective *E*=*E* bond lengths. Values in parentheses correspond to tetrel dumbbells in Li<sub>14</sub>Si<sub>6</sub> and Li<sub>9</sub>Ge<sub>4</sub> which are closest to a double bond system.

For silicides, stannides and plumbides<sup>[12]</sup> as well as pnictogenides<sup>[16]</sup> the situation is similar – quite a few compounds containing dumbbells are known but their electron counts never suggest a true double bond and bond lengths are at least in the range of the elemental single bond.<sup>[17]</sup>

Here, we report on the new Zintl phase Li<sub>3</sub>NaGe<sub>2</sub> which contains anionic dumbbells [Ge<sub>2</sub>]<sup>4-</sup> that appear for the first time in a neat solid with a short Ge-Ge distance that can be characterized as truly double bonded. Furthermore, we show the first Raman spectrum of a solid state Ge=Ge double bond. Since it does not possess covalently bonded ligands it constitutes an analog to molecular O<sub>2</sub>. After the recently discovered Li<sub>18</sub>Na<sub>2</sub>Ge<sub>17</sub>,<sup>[18]</sup>

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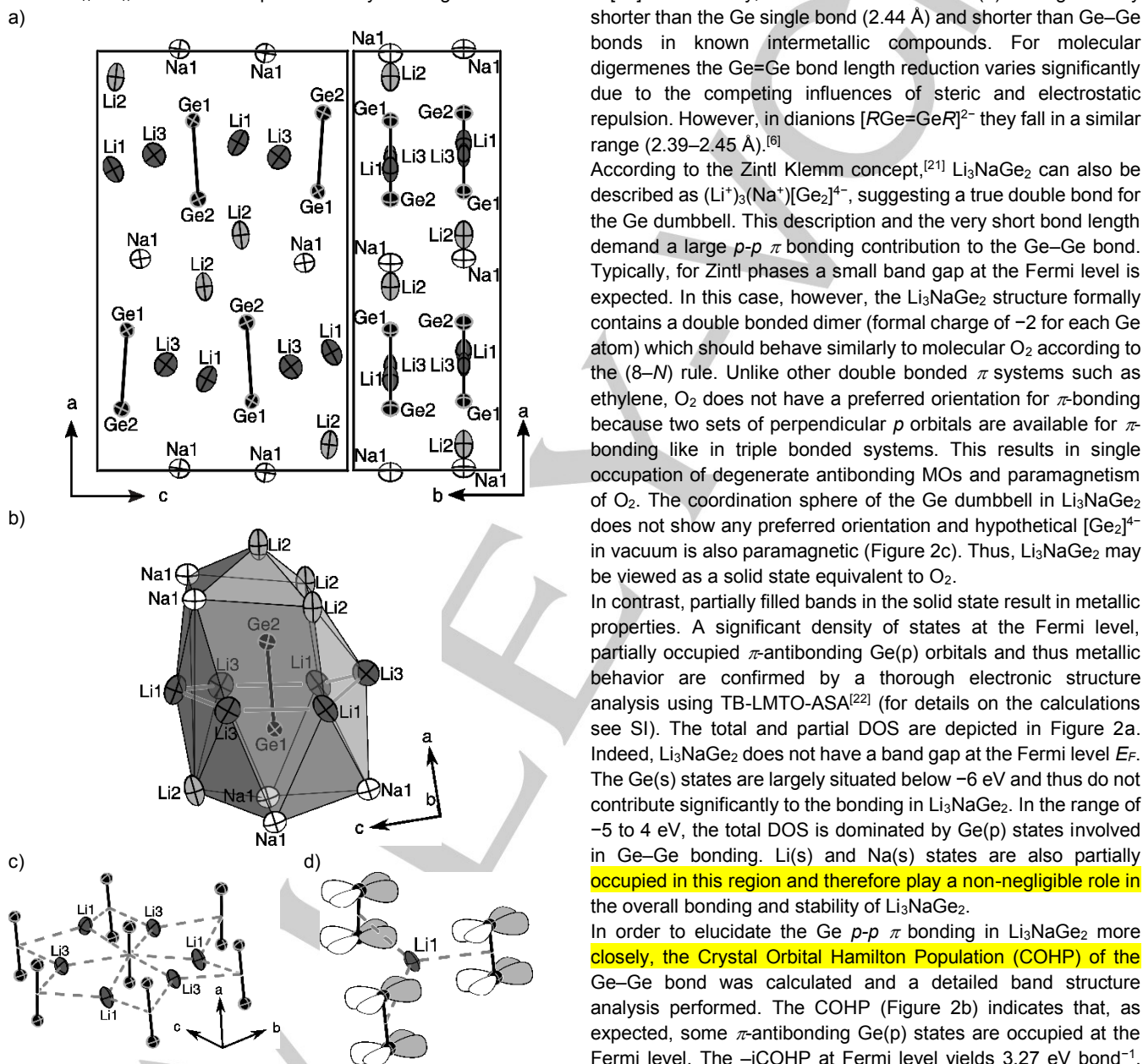
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$\text{Li}_3\text{NaGe}_2$  is only the second compound in the ternary Li-Na-Ge system.

Red, lustrous single crystals of  $\text{Li}_3\text{NaGe}_2$  were initially found as a product of a flux synthesis in the Li-Na-Ge system with excess Na. Subsequently, the air- and moisture-sensitive compound was synthesized directly from the pure elements which were heated up to 750 °C and characterized crystallographically. Nearly phase-pure samples of  $\text{Li}_3\text{NaGe}_2$  were obtained from thoroughly mixed  $\text{Li}_7\text{Ge}_4$ , NaGe and Ge precursors by dwelling at 400 °C.



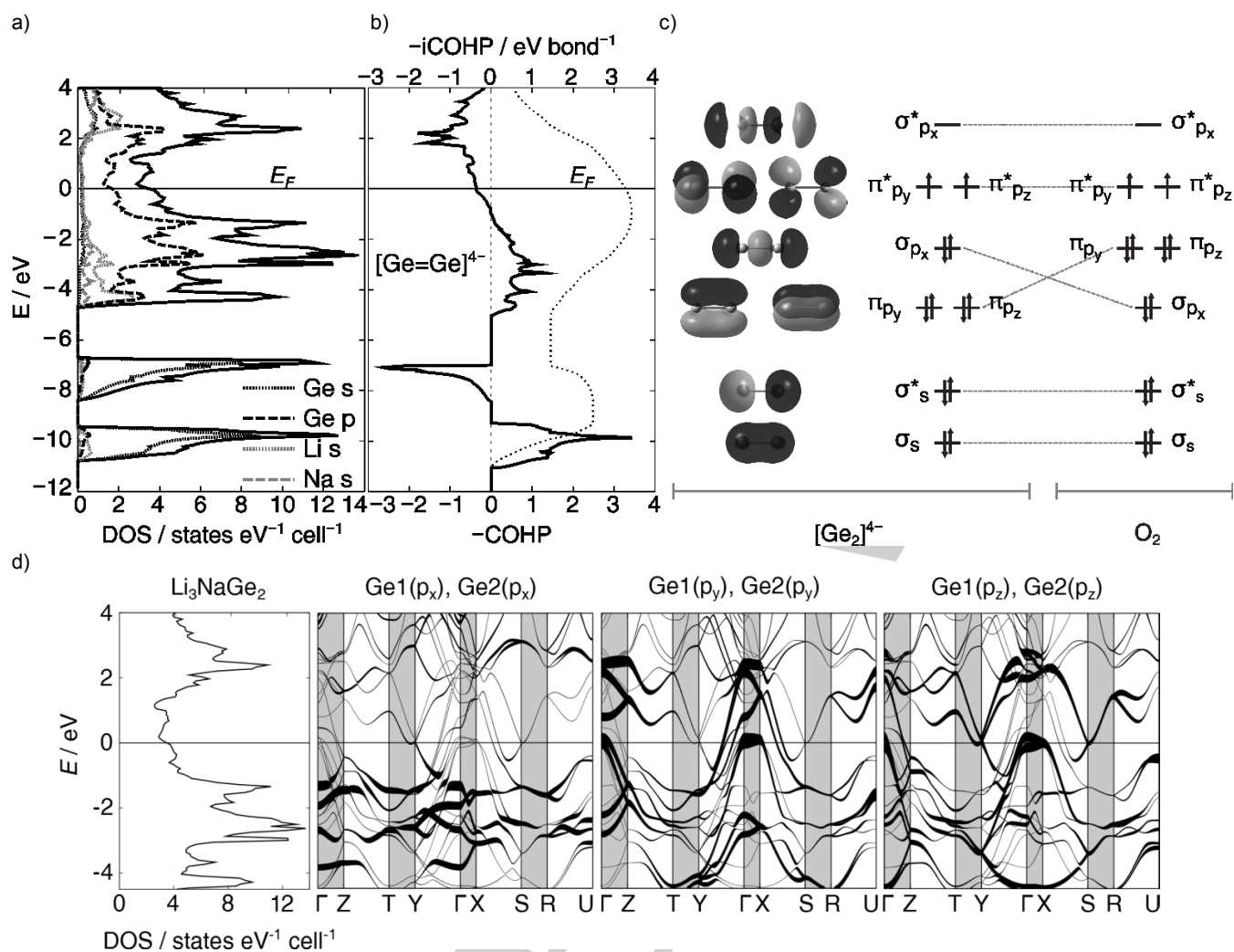
$\text{Li}_3\text{NaGe}_2$  crystallizes in a new structure type in the orthorhombic space group  $Pnma$  (No. 62) with  $a = 12.706(3)$  Å,  $b = 4.4571(9)$  Å,  $c = 7.7715(16)$  Å (Figure 1a).<sup>[20]</sup> The structure contains Ge–Ge dumbbells which are coordinated by 15 alkali metal cations (Figure 1b).

Three Li1 and three Li3 atoms form a six-membered ring in envelope configuration surrounding the dimer. Four Li2 and five Na1 atoms coordinate the Ge atoms in a terminal fashion. Selected distances for the Ge–Ge coordination sphere are given in [19]. Remarkably, the Ge–Ge bond of 2.390(1) Å is significantly shorter than the Ge single bond (2.44 Å) and shorter than Ge–Ge bonds in known intermetallic compounds. For molecular digermenes the Ge=Ge bond length reduction varies significantly due to the competing influences of steric and electrostatic repulsion. However, in dianions  $[\text{RGe}=\text{GeR}]^{2-}$  they fall in a similar range (2.39–2.45 Å).<sup>[6]</sup>

According to the Zintl Klemm concept,<sup>[21]</sup>  $\text{Li}_3\text{NaGe}_2$  can also be described as  $(\text{Li}^+)_3(\text{Na}^+)[\text{Ge}_2]^{4-}$ , suggesting a true double bond for the Ge dumbbell. This description and the very short bond length demand a large  $p$ - $p$   $\pi$  bonding contribution to the Ge–Ge bond. Typically, for Zintl phases a small band gap at the Fermi level is expected. In this case, however, the  $\text{Li}_3\text{NaGe}_2$  structure formally contains a double bonded dimer (formal charge of –2 for each Ge atom) which should behave similarly to molecular  $\text{O}_2$  according to the  $(8-N)$  rule. Unlike other double bonded  $\pi$  systems such as ethylene,  $\text{O}_2$  does not have a preferred orientation for  $\pi$ -bonding because two sets of perpendicular  $p$  orbitals are available for  $\pi$ -bonding like in triple bonded systems. This results in single occupation of degenerate antibonding MOs and paramagnetism of  $\text{O}_2$ . The coordination sphere of the Ge dumbbell in  $\text{Li}_3\text{NaGe}_2$  does not show any preferred orientation and hypothetical  $[\text{Ge}_2]^{4-}$  in vacuum is also paramagnetic (Figure 2c). Thus,  $\text{Li}_3\text{NaGe}_2$  may be viewed as a solid state equivalent to  $\text{O}_2$ .

In contrast, partially filled bands in the solid state result in metallic properties. A significant density of states at the Fermi level, partially occupied  $\pi$ -antibonding Ge( $p$ ) orbitals and thus metallic behavior are confirmed by a thorough electronic structure analysis using TB-LMTO-ASA<sup>[22]</sup> (for details on the calculations see SI). The total and partial DOS are depicted in Figure 2a. Indeed,  $\text{Li}_3\text{NaGe}_2$  does not have a band gap at the Fermi level  $E_F$ . The Ge( $s$ ) states are largely situated below –6 eV and thus do not contribute significantly to the bonding in  $\text{Li}_3\text{NaGe}_2$ . In the range of –5 to 4 eV, the total DOS is dominated by Ge( $p$ ) states involved in Ge–Ge bonding. Li( $s$ ) and Na( $s$ ) states are also partially occupied in this region and therefore play a non-negligible role in the overall bonding and stability of  $\text{Li}_3\text{NaGe}_2$ .

In order to elucidate the Ge  $p$ - $p$   $\pi$  bonding in  $\text{Li}_3\text{NaGe}_2$  more closely, the Crystal Orbital Hamilton Population (COHP) of the Ge–Ge bond was calculated and a detailed band structure analysis performed. The COHP (Figure 2b) indicates that, as expected, some  $\pi$ -antibonding Ge( $p$ ) states are occupied at the Fermi level. The –iCOHP at Fermi level yields 3.27 eV bond<sup>–1</sup>, affirming the large  $p$ - $p$   $\pi$  bonding contribution. For comparison, Ge dumbbells in  $\text{Ae}_7\text{Ge}_6$  (Ae = Ca, Sr, Ba) which have been proven to feature significant  $\pi$  bonding exhibit –iCOHPs of 2.48 to 2.92 eV.<sup>[23]</sup>



**Figure 2.** a) Total and partial DOS curves in the range of -12 eV to 4 eV for  $\text{Li}_3\text{NaGe}_2$  (total: solid black, Ge1(s), Ge2(s): dotted black, Ge1(p), Ge2(p): dashed black, Li1(s), Li2(s), Li3(s): dotted grey, Na1(s): dashed grey); b) COHP (solid line) and integrated COHP (dotted line) of the Ge1–Ge2 bond in  $\text{Li}_3\text{NaGe}_2$ ,  $i\text{COHP}$  at  $E_F = 3.27 \text{ eV bond}^{-1}$ ; c) molecular orbital pictures of free  $[\text{Ge}_2]^{4-}$  and schematic MO diagrams of free  $[\text{Ge}_2]^{4-}$  and  $\text{O}_2$  calculated at the DFT-PBE0/def2-TZVP level of theory (s. SI, the  $p_x$  orbital is chosen to be parallel to the bond axis as in  $\text{Li}_3\text{NaGe}_2$ ); d) total DOS curve as well as band structures including Ge(p) fatbands in the range of -4.5 eV to 4 eV for  $\text{Li}_3\text{NaGe}_2$ .

A fatband analysis of the Ge(p) states serves to clarify the  $\pi$  bonding situation of  $[\text{Ge}_2]^{4-}$  (Figure 2d). Although the Ge dumbbell is not aligned exactly with any cell parameter, a separate view of the  $p_x$ ,  $p_y$ , and  $p_z$  orbital contributions clearly shows that the Ge anion may justifiably be related to molecular  $\text{O}_2$ : The  $p_x$  orbitals are oriented almost parallel to the Ge–Ge bond and the corresponding bands are all located below  $E_F$ , representing the Ge–Ge  $\sigma$  bond. The  $p_y$  and  $p_z$  orbitals are oriented nearly perpendicular to the bond axis and are therefore available for  $\pi$  bonding. The corresponding bands are located around  $E_F$ , demonstrating a significant  $\pi$  bonding contribution. As also seen in the COHP analysis, the  $\pi$ -antibonding  $p_y$  and  $p_z$  bands are partially occupied, similar to molecular  $\text{O}_2$ .

According to magnetic measurements (see SI),  $\text{Li}_3\text{NaGe}_2$  is diamagnetic with a molar magnetic susceptibility of  $-4.0 \times 10^{-5} \text{ emu/mol}$  at 5000 Oe, suggesting that the diamagnetic

contributions of  $\text{Li}^+$ ,  $\text{Na}^+$ , and the Ge core and 3d electrons superimpose Pauli-paramagnetic contributions from the conduction electrons of the metal.<sup>[24]</sup>

The Raman spectrum of  $\text{Li}_3\text{NaGe}_2$  is shown in Figure 3. We assigned the Raman bands by utilizing density functional calculations (DFT-PBE/TZVP level of theory, see SI for full computational details). It was not possible to calculate Raman intensities because  $\text{Li}_3\text{NaGe}_2$  shows metallic conductivity, but calculating the wavenumbers of the Raman active modes and inspecting the corresponding normal modes still enabled the complete interpretation of the spectrum (Table S1). The broad band centered at about  $350 \text{ cm}^{-1}$  arises from vibrational motion of the Li atoms. The  $230 \text{ cm}^{-1}$  band is due to Ge=Ge stretching vibrations of the Ge dumbbell. The calculated wavenumbers are slightly overestimated in comparison to experiment, showing one symmetric Ge=Ge stretching mode at  $251 \text{ cm}^{-1}$  and two asymmetric stretching modes at  $230$  and  $224 \text{ cm}^{-1}$ .<sup>[25]</sup> This

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stretching frequency is in the range known from Zintl polyanions such as  $[\text{Ge}_9]^{4-}$  ( $220\text{--}222\text{ cm}^{-1}$ ) and  $[\text{Ge}_4]^{4-}$  ( $274\text{ cm}^{-1}$ ).<sup>[26]</sup> Finally, the band centered at  $90\text{ cm}^{-1}$  is due to tilting and low-energy motion of the Ge dumbbell and falls in the range of libration modes of  $[\text{Ge}_9]^{4-}$  clusters.<sup>[27]</sup>

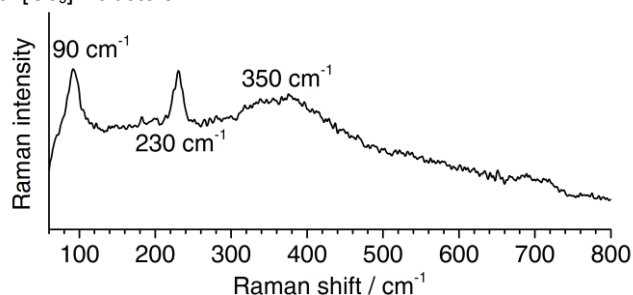


Figure 3. Raman spectrum of a  $\text{Li}_3\text{NaGe}_2$  single crystal.

$^6\text{Li}$  and  $^{23}\text{Na}$  magic angle spinning (MAS) NMR spectra were recorded for  $^6\text{Li}$ -enriched  $\text{Li}_3\text{NaGe}_2$  (Figure 4). The spectra can be consistently interpreted with the aid of 2D  $^6\text{Li}$  spin-exchange,  $^7\text{Li}$  1D and  $^{23}\text{Na}$  MQMAS NMR (Figures S8 to S10) in combination with DFT-PBE calculation of chemical shifts and quadrupolar NMR parameters for  $\text{Na}_7\text{LiGe}_8$  and  $\text{Li}_{14}\text{Ge}_6$  (cf. SI for details on the experiments and calculations Tables S2, S3).

The  $^6\text{Li}$  NMR spectrum contains two major signals at 94.5 and  $-10.0$  ppm with integral ratio 1:2, which belong to  $\text{Li}_3\text{NaGe}_2$ . The nearness of the corresponding Li atom positions in the unit cell is proven by  $^6\text{Li}$  spin-exchange NMR (Figure S9). Negative shifts are known from  $\text{Li}^+$  located in  $\pi$  electron clouds such as in aromatic  $[\text{Ge}_5]^{6-}$  in  $\text{Li}_{12}\text{Ge}_7$  ( $-17\text{ ppm}$ )<sup>[28]</sup> or in the Li cyclopentadienide (Cp) monomer ( $-7.6\text{ ppm}$ )<sup>[29]</sup>. Li1 and Li3 are surrounded by  $\pi$ -electrons of three Ge dumbbells (Figure 1). Therefore, we assign the signal at  $-10.0$  ppm to these two atom positions (Figure 4a). The two Li sites are not resolved due to their similar coordination spheres. The Knight shifted  $^6\text{Li}$  signal at 94.5 ppm can be attributed to Li2 which coordinates the Ge dumbbells terminally (Figure 1b). Minor signals at 1.9 and 28.1 ppm belong to  $\text{Na}_7\text{LiGe}_8$ <sup>[30]</sup> and  $\text{Li}_{14}\text{Ge}_6$ <sup>[31]</sup> impurities, respectively (cf. SI Figure S11 and Table S2).

Apart from minor spinning sidebands, the  $^{23}\text{Na}$  NMR spectrum shows two major and one minor center-band signals (Figure 4b), of which the highest at 315 ppm belongs to Na1 in  $\text{Li}_3\text{NaGe}_2$ . Like Li2, this Na environment has a Knight shift well outside the diamagnetic shift range, which is explained by the fact that it possesses a similar atomic environment and experiences the same local electronic band structure (cf. SI). The signals at  $-8.0$  and  $38.0$  ppm are assigned to the impurity  $\text{Na}_7\text{LiGe}_8$  also observed with  $^6\text{Li}$  NMR. The interpretation of 1D NMR spectra are corroborated by  $^{23}\text{Na}$  MQMAS NMR and DFT-PBE calculations (Figure S10, Tables S2, S3).

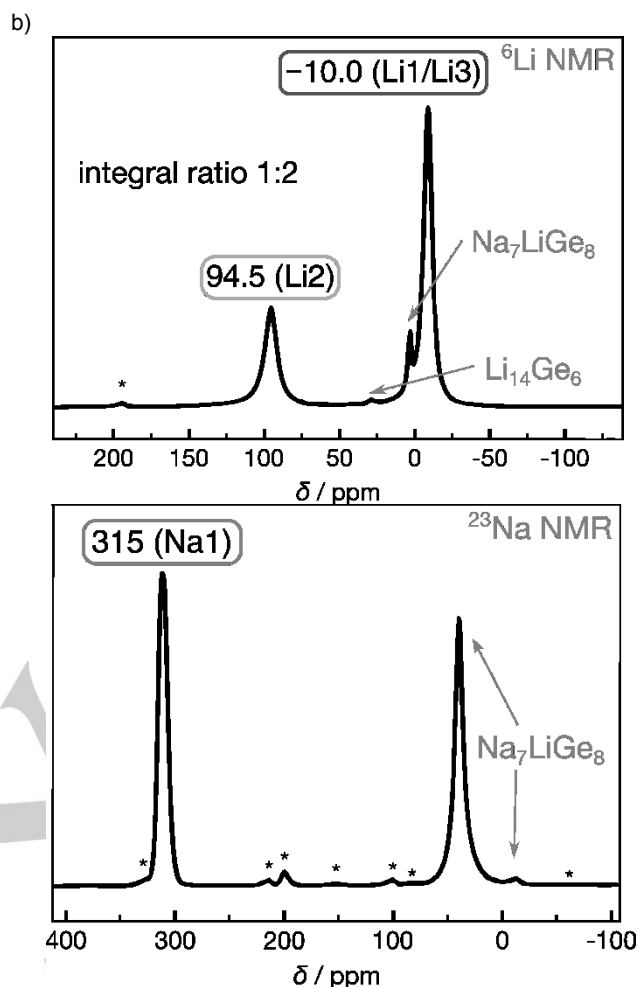


Figure 4. a)  $^6\text{Li}$  and b)  $^{23}\text{Na}$  MAS NMR spectra of  $^6\text{Li}_3\text{NaGe}_2$  (15 kHz MAS spinning speed, 11.7 T, ambient temperature). Signal assignments for the main phase and the respective crystallographic positions in black as well as for the impurity phases in grey. Rotational sidebands are marked by asterisks.

In conclusion, we have discovered the novel phase  $\text{Li}_3\text{NaGe}_2$  which contains  $[\text{Ge}_2]^{4-}$  dumbbells. Ge–Ge distance and electronic structure calculations clearly indicate a true Ge=Ge double bond with a strong influence of its  $\pi$  electron system on  $^6\text{Li}$  NMR shifts.  $\text{Li}_3\text{NaGe}_2$  can be viewed as a model system for heavier element multiple bonds in molecular compounds without preferential orientation of the  $\pi$  bonds, rendering it an example of a solid-state equivalent to molecular  $\text{O}_2$ . The resulting degeneracy of  $\pi$ -bonding  $p$  orbitals which is well known for paramagnetic  $\text{O}_2$  leads to metallic behavior in the title compound.

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**Keywords:** germanium dumbbell • double bond • lithium • sodium • Zintl phases

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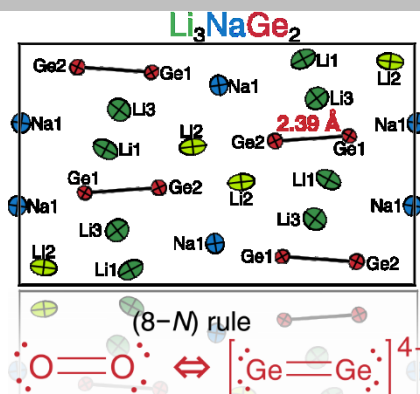
Entry for the Table of Contents (Please choose one layout)

Layout 1:

## COMMUNICATION

### A true double bond in neat solids

between two Ge atoms is observed in  $\text{Li}_3\text{NaGe}_2$  and theoretically established by electronic structure calculations. The p bond character of the  $[\text{Ge}_2]^{4-}$  dumbbells is experimentally confirmed by the upfield  $^6\text{Li}$  NMR shift of the coordinating Li cations. As in molecular  $\text{O}_2$  the  $\pi$ -bonding orbitals have no preferential orientation, are degenerate and partially filled, but are expanded into bands, resulting in



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$[\text{Ge}_2]^{4-}$  Dumbbell with Very Short  
Ge-Ge Distances in the Zintl Phase  
 $\text{Li}_3\text{NaGe}_2$  – a Solid State Equivalent  
to Molecular  $\text{O}_2$