Zintl Phases Very Important Paper

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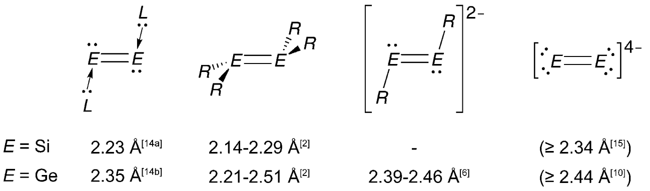
$[Ge_2]^{4-}$ Dumbbells with Very Short Ge−Ge Distances in the Zintl Phase Li_3NaGe_2: A Solid-State Equivalent to Molecular O_2

*Lavinia M. Scherf, Antti J. Karttunen, Oliver Pecher, Pieter C. M. M. Magusin, Clare P. Grey, and Thomas F. Fässler**

Abstract: *The novel ternary Zintl phase Li_3NaGe_2 comprises alkali-metal cations and $[Ge_2]^{4-}$ dumbbells. The diatomic $[Ge_2]^{4-}$ unit is characterized by the shortest Ge−Ge distance (2.390(1) Å) ever observed in a Zintl phase and thus represents the first Ge=Ge double bond under such conditions, 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 ^6Li NMR shift of −10.0 ppm, which was assigned to the Li cations surrounded by the π systems of three Ge dumbbells, further underlines this interpretation. For the unperturbed, ligand-free dumbbell in Li_3NaGe_2, the π-bonding p_y and p_z orbitals are degenerate as in molecular oxygen, which has singly occupied orbitals. The partially filled π-type bands of the neat solid Li_3NaGe_2 cross the Fermi level, resulting in metallic properties. Li_3NaGe_2 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.[1–3] Among those, the heavier tetrel homologues all adopt a *trans*-bent structure in contrast to planar ethylene. The pyramidalization at the E atom in $R_2E{=}ER_2$ drastically influences the possibility of forming a classical π bond between the two metal atoms for E = Ge, Sn, and Pb.

The CGMT model proposed by Trinquier and Malrieu[4] traces the deviation from planarity in $R_2E{=}ER_2$ molecules back to the relative values of the singlet and triplet energies of the monomeric units ER_2 (E_S and E_T, respectively) and the energy of the double-bonded system: For $E_{\sigma+\pi} > 2\Delta E_{S-T}$ a classical planar structure is obtained, whereas $E_{\sigma+\pi} < 2\Delta E_{S-T}$ favors the *trans*-bent structure. $E_{\sigma+\pi} < \Delta E_{S-T}$ results in monomeric ER_2 fragments without E−E bonding.[1,5]



Scheme 1. Types of double-bonded heavier tetrel systems and their respective E=E bond lengths. Values in parentheses correspond to the tetrel dumbbells in $Li_{14}Si_6$ and Li_9Ge_4, which are closest to a double-bond system.

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 second-row elements, double bonds are considerably shorter than the sum of the covalent radii, whereas for the heavier homologues, deviations occur owing to the strict requirements of the bulky ligands that are often used to stabilize the reactive bonds or owing to electrostatic repulsion in the case of charged systems. For example, in $R_2Ge{=}GeR_2$, the Ge−Ge bond lengths are in the range of 2.21 to 2.51 Å,[2] most of them being shorter than a Ge−Ge single bond (2.44 Å), but for $[RGe{=}GeR]^{2-}$, greater bond lengths are observed.[6]

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.[7] Assuming a complete valence electron transfer in $BaMg_2Ge_2$, a 14 valence electron $[Ge{-}Ge]^{6-}$ dumbbell should be obtained. However, the Ge−Ge bond (2.58 Å)[8] is significantly longer than a typical Ge single bond, which was sketchily explained by Coulombic repulsion of the negatively charged atoms. Recently, the strong interaction of alkaline-earth metal d states with anions in Zintl phases was experimentally established, hinting at a less effective electron transfer with alkaline-earth metal counterions.[9]

Ge dumbbells also occur in binary lithium germanides, Li_xGe_{1-x} ($0.692 \leq x \leq 0.778$).[10–13] However, assuming the formal electron transfer according to the Zintl–Klemm concept, they never contain a truly double-bonded dumbbell, $[Ge{=}Ge]^{4-}$. Instead, more highly charged species, such as $(Li^+)_{13}(Ge^{4-})_2[Ge_2]^{5-}$ for $Li_{13}Ge_4$ and $(Li^+)_9([Ge_2]^{4.5-})_2$ for Li_9Ge_4 have been considered, or alternatively $[Ge_2]^{4-}$ units with one or 0.5 excess electrons per dimer, respectively, have been proposed. Yet, with decreasing Li content, π-bonding contributions are expected to increase, and the Ge−Ge bond lengths accordingly decrease from 2.62 Å ($Li_{13}Ge_4$)[12,13] to 2.44 Å (Li_9Ge_4),[10] but in all cases, they remain longer than a typical Ge−Ge single bond.

For silicides, stannides, and plumbides[12] as well as pnicogenides,[16] the situation is similar; quite a few com-

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[*] L. M. Scherf, Prof. Dr. T. F. Fässler
Department of Chemistry, Technische Universität München
Lichtenbergstrasse 4, 85747 Garching/München (Germany)
E-mail: thomas.faessler@lrz.tum.de

Prof. Dr. A. J. Karttunen
Department of Chemistry, Aalto University
00076 Aalto (Finland)

Dr. O. Pecher, Dr. P. C. M. M. Magusin, Prof. Dr. C. P. Grey
Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge, CB2 1EW (UK)

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pounds containing dumbbells are known but their electron counts never suggest a true double bond, and the bond lengths are at least in the range of the elemental single bond.[17]

Herein, we report on the new Zintl phase, Li_3NaGe_2, which contains anionic dumbbells $[Ge_2]^{4-}$ with a short Ge–Ge bond that can be characterized as a true double bond. To the best of our knowledge, this is the first time that a true Ge=Ge bond has been observed in a neat solid. Furthermore, we show the first Raman spectrum of a solid-state Ge=Ge double bond. As it does not possess covalently bonded ligands, it can be considered as an analogue to molecular O_2. After the recently discovered $Li_{18}Na_2Ge_{17}$,[18] Li_3NaGe_2 is only the second ternary Li/Na/Ge compound to be reported.

Red, lustrous single crystals of Li_3NaGe_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 by heating to 750 °C and characterized crystallographically. Nearly phase-pure samples of Li_3NaGe_2 were obtained from thoroughly mixed $Li_{17}Ge_4$, NaGe, and Ge precursors by dwelling at 400 °C.

Li_3NaGe_2 crystallizes with a new structure type in the orthorhombic space group *Pnma* (No. 62) with $a = 12.706(3)$ Å, $b = 4.4571(9)$ Å, and $c = 7.7715(16)$ Å (Figure 1 a).[20] The structure contains Ge–Ge dumbbells that are coordinated by 15 alkali metal cations (Figure 1 b). Three Li1 and three Li3 atoms form a six-membered ring in envelope configuration that surrounds 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 Ref. [19]. Remarkably, the Ge–Ge bond (2.390(1) Å) is significantly shorter than a Ge single bond (2.44 Å) and shorter than the Ge–Ge bonds in known intermetallic compounds. For molecular digermenes, the Ge=Ge bond-length reduction varies significantly depending on the competing influences of steric and electrostatic repulsion. However, in dianions, $[RGe{=}GeR]^{2-}$, the bond lengths are in a similar range (2.39–2.45 Å).[6]

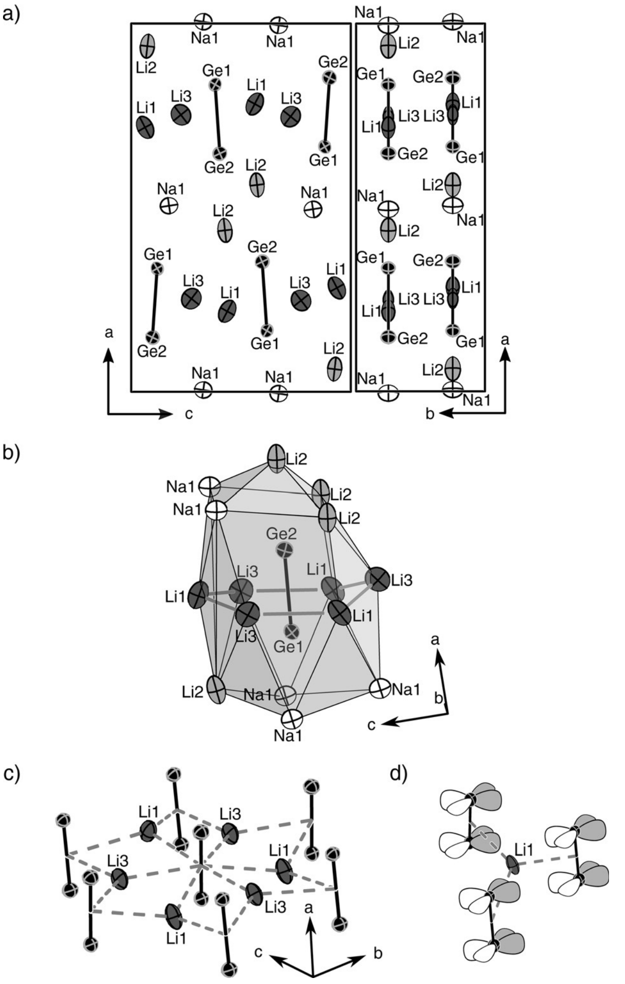

Figure 1. a) Projections of the unit cell of Li_3NaGe_2 onto the *ac* (left) and *ab* planes (right). b, c) Coordination spheres of a Ge–Ge dumbbell (b) and of Li1 and Li3 (c). d) Li1 surrounded by π-bonding Ge p orbitals (thermal ellipsoids set at 90% probability at 123 K).[19]

According to the Zintl–Klemm concept,[21] Li_3NaGe_2 can also be described as $(Li^+)_3(Na^+)[Ge_2]^{4-}$, suggesting a true double bond for the Ge dumbbell. This description and the very short bond length demand a large p–p π-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 Li_3NaGe_2 structure formally contains a double-bonded dimer (a formal charge of −2 for each Ge atom), and the compound should thus behave similarly to molecular O_2 according to the $(8-N)$ rule. Unlike other double-bonded π systems such as ethylene, O_2 does not have a preferred orientation for π bonding because two sets of perpendicular p orbitals are available for π bonding as in triple-bonded systems. This results in the single occupation of degenerate antibonding molecular orbitals (MOs) and paramagnetism. The coordination sphere of the Ge dumbbell in Li_3NaGe_2 does not show any preferred orientation, and hypothetical $[Ge_2]^{4-}$ in vacuum is also paramagnetic (Figure 2 c). Thus, Li_3NaGe_2 may be viewed as a solid-state equivalent to O_2. Li_3NaGe_2 is not, however, paramagnetic, the partially filled bands in the solid state resulting in metallic properties. A significant density of states at the Fermi level, partially occupied π-antibonding Ge(p) orbitals, and thus metallic behavior were confirmed by a thorough electronic-structure analysis by TB-LMTO-ASA[22] (for details on the calculations, see the Supporting Information). The total and partial densities of states (DOS) are depicted in Figure 2 a. Indeed, Li_3NaGe_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 Li_3NaGe_2. In the range of −5 to 4 eV, the total DOS is dominated by the Ge(p) states involved in Ge–Ge bonding. The 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 Li_3NaGe_2.

To analyze the Ge p–p π bonding in Li_3NaGe_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 2 b) indicates that as expected, some π-antibonding Ge(p) states are occupied at the Fermi level. The −iCOHP value at the Fermi level yields 3.27 eV per bond, affirming the large p–p π bonding contri-

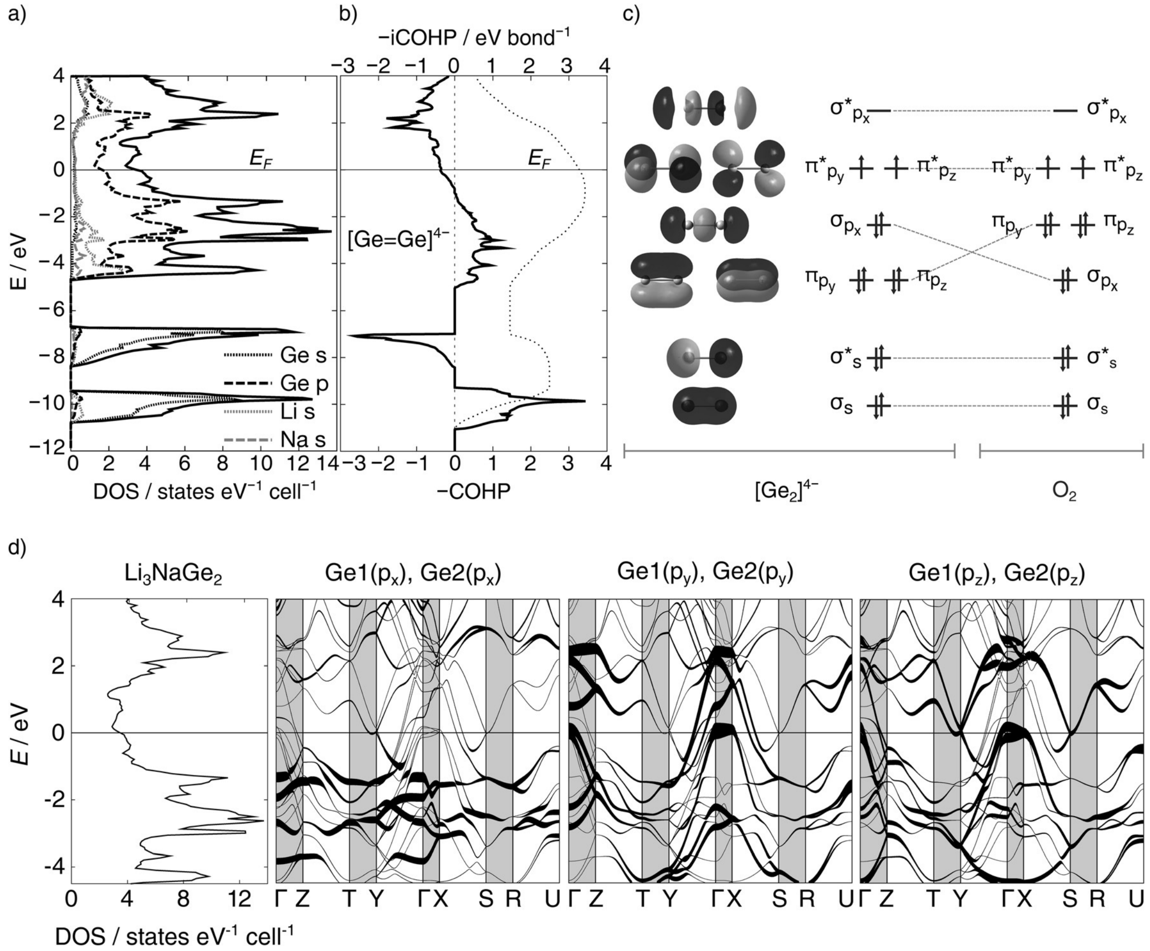

Figure 2. a) Total and partial DOS curves in the range of −12 eV to 4 eV for Li_3NaGe_2. b) COHP (——) and integrated COHP (•••••) of the Ge1−Ge2 bond in Li_3NaGe_2, iCOHP at $E_F = 3.27$ eV per bond. c) Molecular orbitals of free $[Ge_2]^{4-}$ and MO diagrams for free $[Ge_2]^{4-}$ and O_2 calculated at the DFT-PBE0/def2-TZVP level of theory (see the Supporting Information; the p_x orbital was chosen to be parallel to the bond axis as in Li_3NaGe_2). d) Total DOS curve as well as band structures including the Ge(p) fat bands in the range of −4.5 eV to 4 eV for Li_3NaGe_2.

bution. For comparison, Ge dumbbells in M_7Ge_6 (M = Ca, Sr, Ba), which have been shown to feature significant π bonding, exhibit −iCOHP values of 2.48 to 2.92 eV.[23]

A fat-band analysis of the Ge(p) states served to clarify the π-bonding situation of $[Ge_2]^{4-}$ (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 O_2: The p_x orbitals are oriented almost parallel to the Ge−Ge bond. The corresponding bands representing the Ge−Ge σ bond are clearly separated with bonding bands below and antibonding bands well above E_F. The p_y and p_z orbitals are oriented nearly perpendicular to the bond axis and are therefore available for π bonding. The corresponding bands are located around E_F, demonstrating a significant π-bonding contribution. As also seen in the COHP analysis, the π-antibonding p_y and p_z bands are partially occupied, similar to those in molecular O_2.

According to magnetic measurements (see the Supporting Information), Li_3NaGe_2 is diamagnetic with a molar magnetic susceptibility of -4.0×10^{-5} emu mol^{-1} at 5000 Oe, suggesting that the diamagnetic contributions of Li^+, Na^+, and the Ge core and 3d electrons superimpose Pauli paramagnetic contributions from the conduction electrons of the metal.[24]

The Raman spectrum of Li_3NaGe_2 is shown in Figure 3. We assigned the Raman bands by utilizing density functional calculations (DFT-PBE/TZVP level of theory, see the Supporting Information for full computational details). It was not possible to calculate Raman intensities because Li_3NaGe_2 shows metallic conductivity, but by calculating the wavenumbers of the Raman-active modes and inspecting the corresponding normal modes, the spectrum could still be fully interpreted (Supporting Information, Table S1). The broad

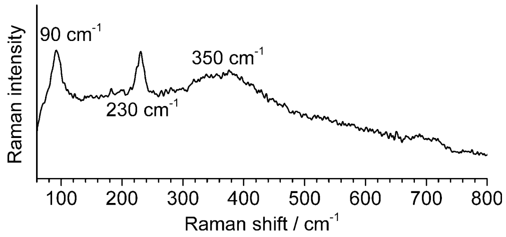

Figure 3. Raman spectrum of a Li_3NaGe_2 single crystal.

band centered at about 350 cm^{-1} arises from vibrational motion of the Li atoms. The 230 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 cm^{-1} and two asymmetric stretching modes at 230 and 224 cm^{-1}.[25] This stretching frequency is in the range typical for Zintl polyanions, such as $[Ge_9]^{4-}$ (220–222 cm^{-1}) and $[Ge_4]^{4-}$ (274 cm^{-1}).[26] Finally, the band centered at 90 cm^{-1} is due to tilting and low-energy motions of the Ge dumbbell and falls in the range of libration modes of $[Ge_9]^{4-}$ clusters.[27]

^{6}Li and ^{23}Na magic angle spinning (MAS) NMR spectra were recorded for ^{6}Li-enriched Li_3NaGe_2 (Figure 4). The spectra can be consistently interpreted with the aid of 2D ^{6}Li spin exchange, ^{7}Li 1D, and ^{23}Na multiple-quantum (MQ) MAS NMR spectroscopy (Figures S8–S10) in combination with DFT-PBE calculations of the chemical shifts and quadrupolar NMR parameters for Na_7LiGe_8 and $Li_{14}Ge_6$ (see the Supporting Information for details and Tables S2, S3).

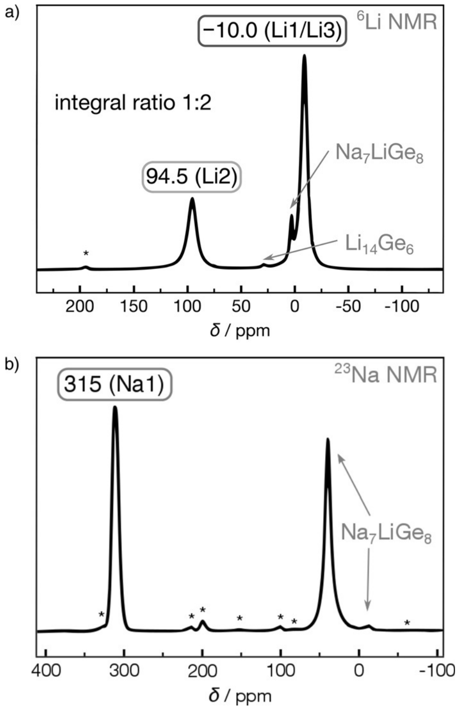

Figure 4. a) ^{6}Li and b) ^{23}Na MAS NMR spectra of $^6Li_3NaGe_2$ (15 kHz MAS spinning speed, 11.7 T, ambient temperature). Signal assignments for the main phase and the respective crystallographic positions are given in black, those for the impurity phases are shown in gray. Rotational sidebands are marked by asterisks.

The ^{6}Li NMR spectrum contains two major resonances at 94.5 and −10.0 ppm with an integral ratio of 1:2, which belong to Li_3NaGe_2. ^{6}Li spin-exchange NMR spectroscopy confirms that the corresponding Li atoms are in close proximity and originate from the same phase (Figure S9). Negative shifts have been reported for Li^+ located in π electron clouds, such as in aromatic $[Ge_5]^{6-}$ in $Li_{12}Ge_7$ (−17 ppm)[28] or in the Li cyclopentadienide (Cp) monomer (−7.6 ppm).[29] Li1 and Li3 are surrounded by the π 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 cannot be resolved owing to their similar coordination spheres. The Knight-shifted ^{6}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 Na_7LiGe_8[30] and $Li_{14}Ge_6$[12,31] impurities, respectively (Figure S11 and Table S2).

Apart from minor spinning sidebands, the ^{23}Na NMR spectrum shows two major and one minor center-band resonances (Figure 4b), of which the highest at 315 ppm belongs to Na1 in Li_3NaGe_2. As for 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 (see the Supporting Information). The signals at −8.0 and 38.0 ppm were assigned to the impurity Na_7LiGe_8, which had also been observed by ^{6}Li NMR analysis. The interpretation of the 1D NMR spectra was corroborated by ^{23}Na MQMAS NMR spectroscopy and DFT-PBE calculations (Figure S10 and Tables S2, S3).

In conclusion, we have discovered that the novel phase Li_3NaGe_2 contains $[Ge_2]^{4-}$ dumbbells. The Ge−Ge distance and electronic-structure calculations clearly indicate a true Ge=Ge double bond, with a strong influence of its π electron system on the ^{6}Li NMR shifts. Li_3NaGe_2 can be viewed as a model system for heavier-element multiple bonds in molecular compounds without preferential orientation of the π bonds, rendering it an example of a solid-state equivalent to molecular O_2. The resulting degeneracy of the π-bonding p orbitals, which is well known for paramagnetic O_2, leads to metallic behavior in the title compound.

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