

Crystal and electronic structures of ScAuGe, CeAuGe, and LuAuGe: a transition from two- to three-dimensional [AuGe] polyanions

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Abstract

New germanides ScAuGe, TmAuGe, and LuAuGe were prepared by melting mixtures of the elements in an arc furnace and subsequent annealing at 1070 K. The structures of ScAuGe and LuAuGe were refined from X-ray single-crystal diffractometer data: $P6_3mc$ (No. 186), $Z = 2$, $a = 430.82(5)$ pm, $c = 684.58(10)$ pm, $V = 0.1100(1)$ nm³, $wR2 = 0.0688$, 275 F_o^2 values, ten variables for ScAuGe; $P6_3mc$ (No. 186), $Z = 2$, $a = 437.75(4)$ pm, $c = 711.38(6)$ pm, $V = 0.1181(1)$ nm³, $wR2 = 0.0340$, 355 F_o^2 values, 11 variables, and a batch scale factor of 0.47(3) for LuAuGe. The lattice constants for TmAuGe are $a = 439.08(4)$ pm, $c = 716.59(7)$ pm, and $V = 0.1196(1)$ nm³. The crystal structures of these germanides are derived from the $CaIn_2$ -type structure by an ordered arrangement of Au and Ge atoms at the indium position. The crystal chemistry of ScAuGe and LuAuGe is compared with that of the recently reported cerium compound. Although the Au–Ge intralayer distances at 259.6 pm in CeAuGe, 260.5 pm in LuAuGe, and 257.6 pm in ScAuGe are similar, the Au–Ge interlayer distances at 364.2 pm in CeAuGe, 292.7 pm in LuAuGe, and 275.2 pm in ScAuGe differ significantly. Thus, the [AuGe] polyanions are changed from two-dimensional layers in CeAuGe to a three-dimensional network of distorted tetrahedra in ScAuGe. Chemical bonding within the structures was investigated by TB-LMTO-ASA band structure calculations. The energy bands, the densities of states and the valence charge densities are discussed. Bonding is characterized by intralayer bonds between Au and Ge within the puckered AuGe hexagons. In addition, in the case of ScAuGe strong bonds are directed from the Au atoms of one layer to the Ge atoms of the neighbouring layer. Weaker interlayer bonding is observed in LuAuGe and no interlayer interaction in CeAuGe, as already indicated by the pronounced increase of the interlayer distances.

Keywords: ScAuGe; CeAuGe; LuAuGe; Crystal structure; Electronic structure calculations

1. Introduction

Several equiatomic intermetallic phases of rare earth elements with a transition metal and an element of the p block form structures related to the well known AlB_2 -type [1,2]. The main features, as well as several substitution and deformation derivatives of the AlB_2 -type structure, were discussed in detail by Gladyshevskii et al. [3]. Recently, Rossi et al. [4] characterized a series of $LnAuGe$ ($Ln = Y, La-Nd, Sm, Gd-Er, Yb$) compounds by X-ray powder diffraction. They claimed these germanides adopted the $LiGaGe$ -type structure [5,6], an ordered derivative of the $CaIn_2$ type [7], which itself can be described as a puckered derivative of the AlB_2 structure.

In the course of our studies on AlB_2 -related intermetallics [8–11] we synthesized ScAuGe, TmAuGe, and LuAuGe, three new members of the $LnAuGe$

series. The crystal structure and physical properties of CeAuGe were reported previously [11]. EuAuGe, recently described by us, is not isotopic with these compounds. It crystallizes with a new ordered version of the $CeCu_2$ -type structure [12].

2. Sample preparation and lattice constants

Starting materials for the preparation of the ternary germanides were ingots of the rare earth metals (Johnson Matthey), gold wire (Degussa), and germanium lumps (Wacker), all with stated purities better than 99.9%. Samples were prepared by arc-melting mixtures of the elemental constituents in 1:1:1 atomic ratio in an argon atmosphere. The argon was purified over molecular sieves, titanium sponge (900 K), and an oxysorb catalyst [13]. The melted buttons were

Table 1
Lattice constants of the hexagonal germanides LnAuGe

Compound	<i>a</i> (pm)	<i>c</i> (pm)	<i>c/a</i>	<i>V</i> (nm ³)	Reference
ScAuGe	430.82(5)	684.58(10)	1.589	0.1100(1)	This work
CeAuGe	446.03(7)	793.60(12)	1.779	0.1367(1)	[11]
TmAuGe	439.08(4)	716.59(7)	1.632	0.1196(1)	This work
LuAuGe	437.75(4)	711.38(6)	1.625	0.1181(1)	This work

turned over and remelted three times from each side to ensure homogeneity. The total weight loss after this procedure was always smaller than 0.5%. The buttons were subsequently enclosed in evacuated silica tubes and annealed at 1070 K for 10 days. All melted and annealed buttons had a light grey colour, while the compounds are dark grey in powdered form. Single crystals show metallic lustre and are stable in air.

The lattice constants (see Table 1) were derived from a least squares fit of Guinier powder data [14]. Cu $K\alpha_1$ radiation ($\lambda = 154.056$ pm) was used and 99.999% silicon ($a = 543.07$ pm) as an internal standard. The indexing of the diffraction patterns was facilitated by intensity calculations [15] using the parameters from the single crystal structure refinements.

3. Electronic structure calculations

Self-consistent ab initio band structure calculations for ScAuGe, CeAuGe, and LuAuGe were performed with the TB-LMTO-ASA method [16,17] in its scalar relativistic version. Thus, all relativistic effects except spin orbit coupling were taken into account. The local exchange-correlation potential of Barth and Hedin [18] was used. As the LMTO-method was described elsewhere [19], only some details of the particular calculations are given here. All k-space integrations were performed with the tetrahedron method [20] using 296 irreducible k-points within the Brillouin zone (Fig. 1). The basis sets consisted of 6s, 5d and 4f orbitals for Lu and Ce, 4s and 3d orbitals for Sc, 6s, 6p and 5d orbitals for gold and 4s and 4p orbitals for Ge. The 6p orbitals for Lu and Ce, the 4p orbital for Sc, the 5f ones for gold and the 4d ones for Ge were treated by the downfolding technique; inner electrons as soft core. Since the present structures are rather open, special care was taken in filling the interatomic space with interstitial spheres (E). This was done using an automatic procedure developed by Krier et al. [21], which also determines atomic and interstitial sphere radii. The optimal position of an interstitial sphere was at $1/3, 2/3, 0$ in the Wigner–Seitz cell. The resulting radii of the different spheres were found to be $s_{\text{Sc}} = 3.38$, $s_{\text{Au}} = 2.85$, $s_{\text{Ge}} = 2.81$, $s_{\text{E}} = 1.66$ for ScAuGe,

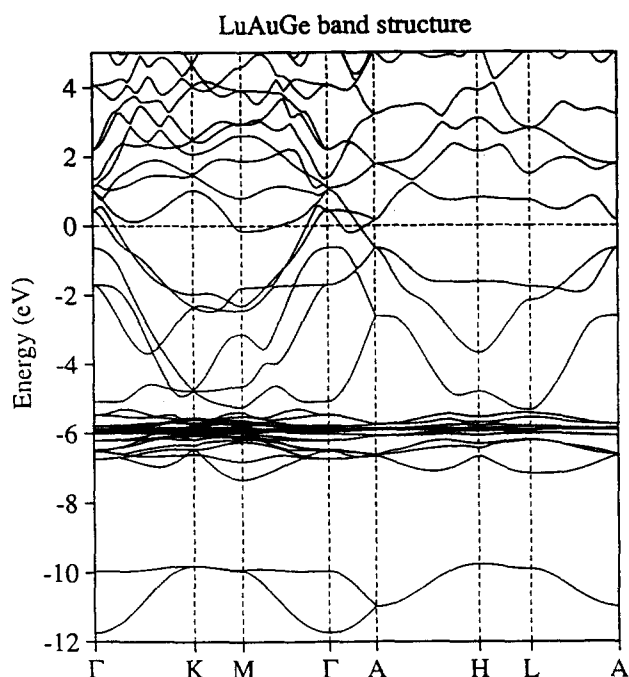
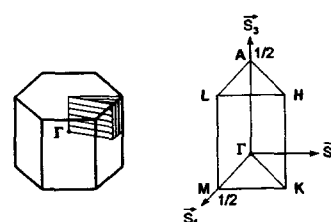


Fig. 1. High symmetry points of the Brillouin zone and electronic structure of LuAuGe.

$s_{\text{Ce}} = 3.97$, $s_{\text{Au}} = 2.81$, $s_{\text{Ge}} = 2.78$, $s_{\text{E}} = 1.59$ for CeAuGe, and $s_{\text{Lu}} = 3.53$, $s_{\text{Au}} = 2.86$, $s_{\text{Ge}} = 2.83$, $s_{\text{E}} = 1.73$ for LuAuGe, which resulted in a maximum overlap of 16% between any two spheres. For ferromagnetic CeAuGe a spin polarized calculation was also performed.

4. Structure refinements

Single crystals of ScAuGe and LuAuGe were selected from the crushed buttons after the annealing

process and investigated by Buerger precession photographs in order to check their symmetry and suitability for intensity data collection. The photographs showed hexagonal Laue symmetry $6/mmm$, and the systematic extinctions (hhl only observed with $l = 2n$, $00l$ only with $l = 2n$) led to the possible space groups $P6_3mc$, $P\bar{6}2c$, and $P6_3/mmc$, of which $P6_3mc$ (No.186) was found to be correct during structure refinement. This finding is in agreement with the earlier suggestions from powder data reported by Rossi et al. [4].

Intensity data were collected on a four-circle diffractometer (CAD4) with graphite monochromatized Ag $K\alpha$ radiation and a scintillation counter with pulse-height discrimination. Crystallographic data and some details of the data collections are summarized in Table 2.

The structures were refined using SHELXL-93 [22] with anisotropic displacement parameters for all atoms. In the refinement of LuAuGe the calculated Flack parameter [23,24] had a value of about one-half, indicating twinning by inversion. This was recently also observed for CeAuGe [11]. Therefore, the inversion twin matrix ($\bar{1}00, 010, 001$) was introduced and a batch scale factor (BASF) was refined. The refinement converged to significantly lower residuals and

improved standard deviations. In contrast, the ScAuGe crystal was not twinned (see Flack parameters in Table 2). For the refinement of LuAuGe, two reflections with $F_o^2 < -2\sigma(F_o^2)$ ($\bar{1}51$ and 033) were treated as unobserved. Final difference Fourier analyses were flat in both refinements. Atomic parameters and interatomic distances are listed in Tables 3 and 4.

Table 3
Atomic coordinates and isotropic displacement parameters (pm^2) for ScAuGe and LuAuGe

Atom	Wyckoff site	x	y	z	U_{eq}^a
ScAuGe					
Sc	2a	0	0	0.0012(5)	84(6)
Au	2b	1/3	2/3	0.7000 ^b	89(2)
Ge	2b	1/3	2/3	0.2980(3)	75(4)
LuAuGe					
Lu	2a	0	0	0.99410(8)	74(1)
Au	2b	1/3	2/3	0.7000 ^b	90(1)
Ge	2b	1/3	2/3	0.2886(1)	66(2)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b Owing to the small number of parameters, an automatic restraint of the floating origin is not possible [25].

Table 2
Crystal data and structure refinement for ScAuGe and LuAuGe

	ScAuGe	LuAuGe
Empirical formula	ScAuGe	LuAuGe
Formula weight (g mol^{-1})	314.52	444.53
Temperature (K)	293(2)	293(2)
Wavelength (μm)	56.086	56.086
Crystal system	hexagonal	hexagonal
Space group	$P6_3mc$	$P6_3mc$
Unit cell dimensions	see Table 1	see Table 1
Formula units per cell	$Z = 2$	$Z = 2$
Calculated density (g cm^{-3})	9.49	12.51
Crystal size (μm^3)	$25 \times 50 \times 50$	$20 \times 25 \times 50$
Absorption correction	from ψ -scan data	from ψ -scan data
Transmission ratio (max/min)	1:0.379	1:0.576
Absorption coefficient (mm^{-1})	44.64	62.46
$F(000)$	264	364
θ range for data collection	4.0° to 30.0°	4.0° to 32.0°
Scan type	$\omega/2\theta$	$\omega/2\theta$
Range in hkl	$\pm 5, \pm 7, \pm 12$	$\pm 8, \pm 8, \pm 13$
Total no. reflections	1035	3111
Independent reflections	275 ($R_{int} = 0.0902$)	257 ($R_{int} = 0.0848$)
Reflections with $I > 2\sigma(I)$	257 ($R_\sigma = 0.0568$)	315 ($R_\sigma = 0.0308$)
Refinement method	Full-matrix least squares on F^2	Full matrix least squares on F^2
Data/restraints/parameters	275/0/10	355/0/11
Goodness-of-fit on F^2	1.207	1.157
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0252, wR2 = 0.0664$	$R1 = 0.0143, wR2 = 0.0329$
R indices (all data)	$R1 = 0.0282, wR2 = 0.0688$	$R1 = 0.0201, wR2 = 0.0340$
Extinction coefficient	0.039(4)	0.0108(9)
Largest diff. peak and hole (e nm^{-3})	1219 and -2543	2372 and -1604
twin ratio (BASF)	—	0.47(3)
Flack parameter	$-0.02(5)$	—

Table 4
Interatomic distances (pm) in the structures of ScAuGe and LuAuGe

<i>ScAuGe</i>		<i>LuAuGe</i>	
Sc: 3 Au	283.5(2)	Lu: 3 Ge	292.0(1)
3 Ge	285.0(2)	3 Au	292.1(1)
3 Ge	321.2(3)	3 Au	328.1(1)
3 Au	323.1(2)	3 Ge	328.3(1)
2 Sc	342.3(1)	2 Lu	355.7(1)
6 Sc	430.8(1)	6 Lu	437.8(1)
Au: 3 Ge	257.6(1)	Au: 3 Ge	260.5(1)
1 Ge	275.2(2)	3 Lu	292.1(1)
3 Sc	283.5(2)	1 Ge	292.7(1)
3 Sc	323.1(2)	3 Lu	328.1(1)
Ge: 3 Au	257.6(1)	Ge: 3 Au	260.5(1)
1 Au	275.2(2)	3 Lu	292.0(1)
3 Sc	285.0(2)	1 Au	292.7(1)
3 Sc	321.2(3)	3 Lu	328.3(1)

Listings of the structure factors and the anisotropic displacement parameters are available¹.

5. Results and discussion

5.1. Crystal chemistry

Three new compounds of the isotypic series LnAuGe [4] were obtained for the first time, i.e. ScAuGe, TmAuGe, and LuAuGe. Together with the cerium compound, ScAuGe and LuAuGe are the only compounds in this series where the crystal structure was refined from single-crystal data. TmAuGe and all other compounds were only characterized via X-ray powder patterns [4].

The crystal structures of the investigated germanides (Fig. 2) are best described as derived from the well-known AlB₂-type structure, the rare earth atoms occupying the aluminium positions and forming the

trigonal prisms. The gold and germanium atoms occupy the boron positions in an ordered manner, forming hexagonal nets and centring the trigonal prisms. Consecutive layers are rotated by 60° around the perpendicular *c* axis with respect to each other. However, in contrast to AlB₂, the hexagonal nets are slightly puckered. The structures can, therefore, also be described as ordered derivatives of the CaIn₂-type structure (puckered AlB₂). Considering the rare earth atoms as layer A and the two AuGe networks as layers B and C, the stacking sequence for these compounds can be denoted as ABAC.

The degree of puckering considerably influences the coordination of the atoms and their chemical bonding within and between the networks. While the deviations from planarity are rather small in CeAuGe, they are very pronounced in ScAuGe. Thus, as already suggested by Gladyshevskii et al. [3], one has to consider two ordered ternary variants of CaIn₂ (puckered AlB₂), with respect to the coordination chemistry. One is the LiGaGe [5,6] branch, where the Ga and Ge atoms form a three-dimensional [GaGe]_n network with only slightly distorted GaGe₄ and GeGa₄ tetrahedra (each gallium atom has three germanium neighbours at 256.2 pm and one more germanium neighbour at 257.8 pm and vice versa). The second variant is the NdPtSb [26] branch, where the [PtSb]_n polyanions form a two-dimensional network with only very weak interactions between subsequent [PtSb]_n layers (each platinum atom has three antimony neighbours at 264.7 pm within the layer and a fourth antimony contact at 354.1 pm to the next layer). Although, the atoms in LiGaGe and NdPtSb occupy the same Wyckoff sites in space group *P6₃mc*, one should call their relationship isopointal [27,28] rather than isotypic, in view of the crystal chemical differences.

Both structural branches are also present in the case of the equiatomic LnAuGe compounds. Although, the Au–Ge intralayer distances at 259.6 pm in CeAuGe, 260.5 pm in LuAuGe, and 257.6 pm in ScAuGe are similar, the Au–Ge interlayer distances of 364.2 pm in CeAuGe, 292.7 pm in LuAuGe, and 275.2 pm in ScAuGe differ significantly. Accordingly, the [AuGe]

¹They may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the Registry Nos. CSD-401763 (ScAuGe) and CSD-401764 (LuAuGe).

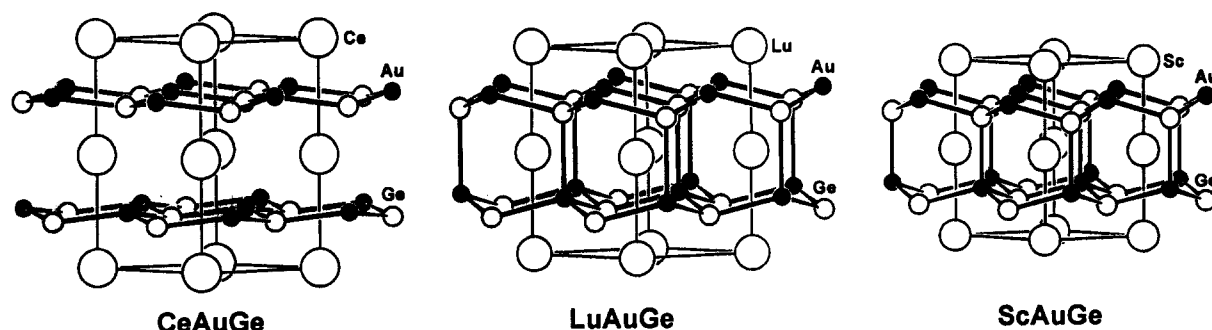


Fig. 2. Crystal structures of CeAuGe, LuAuGe, and ScAuGe.

polyanions change from two-dimensional layers in CeAuGe to a three-dimensional network of distorted tetrahedra in ScAuGe. CeAuGe may therefore be ascribed to the NdPtSb type and ScAuGe to the LiGaGe type respectively. LuAuGe is in between these types.

The intralayer Au–Ge distances in these germanides are significantly smaller than the sum of the metallic radii (281.1 pm) for gold ($r = 144.2$ pm) and germanium ($r = 136.9$ pm), both for coordination number 12 [29]. While the interlayer Au–Ge distance of 275.2 pm in ScAuGe is in the same range, this distance amounts to 292.7 pm in LuAuGe, which is somewhat longer than the sum of the metallic radii. The interlayer Au–Ge distances increase to 364.2 pm in CeAuGe [11] and the AuGe layers are completely separated from each other.

Finally, it is interesting to note that the structures of ScAuGe and ScAuSi [30] are different. Both compounds form ordered structures derived from the CaIn_2 type, both with puckered AuGe and AuSi layers. While these layers are rotated by 60° around the c axis with respect to each other in ScAuGe, they are stacked one upon another in ScAuSi, resulting in Au–Au interactions between the layers.

5.2. Electronic structure

First we will discuss the band structure of LuAuGe (Fig. 1). The Ge–s bands are found about 10 to 12 eV below the Fermi level E_F . A gap of 3 eV separates the Ge–s bands from the bands with mainly Au–d character, which have a width of 2 eV and extend from about 5 to 7 eV below E_F . The Lu–4f states are located around 6 eV below E_F within the range of the Au–d states and they show very little dispersion. For CeAuGe the Ce–4f bands are found at E_F and 1 eV above. There is a small gap between the Au–d states and the conduction band, which consists of the Ge–p bands. The six Ge–p bands are nearly full with only little hole pockets around Γ and A. The band structure, therefore, nearly gaps at the Fermi level and this is the reason for the stability of these three compounds.

The pseudo-gap near E_F may be seen in the total density of states (DOS) of ScAuGe in Fig. 3. This DOS is representative for all three compounds. Although, in the Lu compound the 4f-states appear in the Au–d band range, in the Ce compound the 4f-states start to give contribution just below the Fermi energy.

The DOS at the Fermi energy is $N(E_F) = 1.4$ states/(spin eV) for ScAuGe and $N(E_F) = 0.5$ states/(spin eV) for LuAuGe. The increase of $N(E_F)$ on going from the Lu to the Sc compound is paralleled by an increase of the magnetic susceptibilities (at 300 K) of

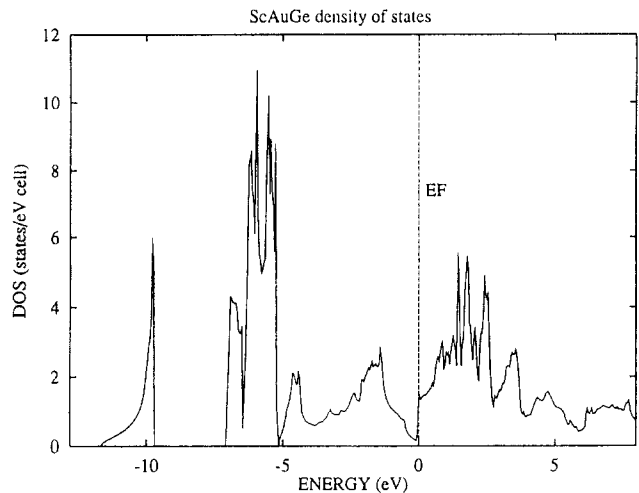


Fig. 3. DOS of ScAuGe.

$-72(1) \times 10^{-6}$ emu mol $^{-1}$ for LuAuGe to $-32(1) \times 10^{-6}$ emu mol $^{-1}$ for ScAuGe, due to an increased Pauli contribution. For details see Ref. [31].

CeAuGe [11] orders ferromagnetically at 10.0 K. Its experimentally determined saturation magnetic moment at 5 K is $1.09(2) \mu_B/\text{Ce}$. We therefore also performed a spin polarized calculation for this compound. The DOS at E_F takes the relatively high value of $N(E_F) = 6$ states/(spin eV) for the paramagnetic calculation and 9 states/(spin eV) for the ferromagnetic calculation. The high density of states of CeAuGe is due to the presence of 4f-electrons at the Fermi level. The spin polarized calculation shows the ferromagnetic ground state to be the stable one with a magnetic energy of 0.8 eV/Ce. The magnetic moment was found to be $1.0 \mu_B/\text{Ce}$, which compares well with the experimental data. This is surprising since, for isotopic CePdP [32–34], a paramagnetic ground state was established by susceptibility measurements and theoretical calculations.

Fig. 4 presents contour plots of the total valence charge distribution of ScAuGe, LuAuGe and CeAuGe. The contour plots show the varying intralayer and interlayer Au–Ge bonding for the different compounds.

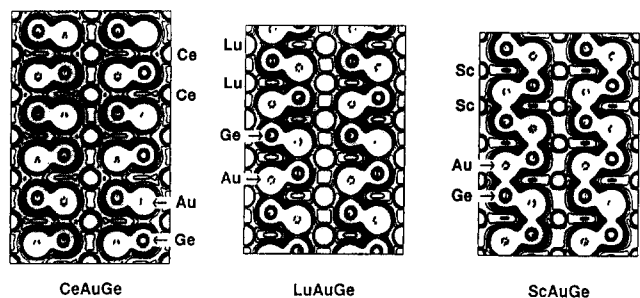


Fig. 4. Total valence charge distribution of ScAuGe, LuAuGe and CeAuGe in the [110] direction ($0.5 \leq x, y < 1.5$): 11 contours are drawn between 0 and $0.04 e/a_0^3$ (a_0 is the Bohr radius).

The electronic charge densities have enabled us to investigate the bonding in these compounds. The main feature is a strong interaction in the puckered AuGe nets. The charge density between the gold and germanium atoms within the *ab* plane is very similar in all three compounds. Perpendicular to the nets the charge density between Au and Ge is slightly higher in LuAuGe than in CeAuGe. We notice a large increase of electronic charge between the AuGe networks for ScAuGe, indicating the presence of covalent bonding.

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