

Donor Layer–Acceptor Chain Formation in the LaNiGe_2 Structure: A Crystallographic and Computational Study

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Synthesis, and single-crystal X-ray diffraction and computational studies were carried out for the title compound. LaNiGe_2 crystallizes in the orthorhombic lattice $Cmcm$ ($a = 4.3040(6)$ Å, $b = 16.892(10)$ Å, $c = 4.2367(5)$ Å, $Z = 4$). It consists of a Ni-capped Ge square lattice and Ge zigzag chains. A unique structural feature is the formation of the square lattice by the more electronegative Ge instead of by Ni atoms as in several other phases such as $\text{La}_3\text{Ni}_4\text{Ge}_4$. Computational analysis indicates that the Ge square lattice acts as an electron donor while the Ge zigzag chain acts as electron acceptor. A donor–acceptor interaction similar to that in the CaBe_2Ge_2 phase stabilizes the Ge square lattice.

Introduction

Ternary intermetallic solid-state compounds of lanthanum, transition metal, and germanium are of continuous interest because of their technological applications, such as in rechargeable cells, and because of their interesting physical properties.^{1–3} Dozens of compounds of the stoichiometry $\text{Ln}_x\text{T}_y\text{Ge}_z$ ($\text{Ln} = \text{lanthanide}$, $\text{T} = \text{transition metal}$) have been synthesized.^{4–11} Many of them crystallize in orthorhombic lattices in which a transition metal forms a square lattice with capping germanium atoms on the square hollows. $\text{La}_3\text{Ni}_4\text{Ge}_4$ exemplifies such a feature. In this solid, Ni forms square lattice layers with Ge capping the squares to form GeNi_4 pyramids (Figure 1).⁷ This structural motif is found in one of the most populous families—the $\text{ThCr}_2\text{-Si}_2$ series.¹² LaNiGe_2 , however, is an exception. In this structure, it is the more electronegative element Ge that makes the square lattice. The main structural motif is the NiGe_4 pyramid (Figure 2). This intriguing feature

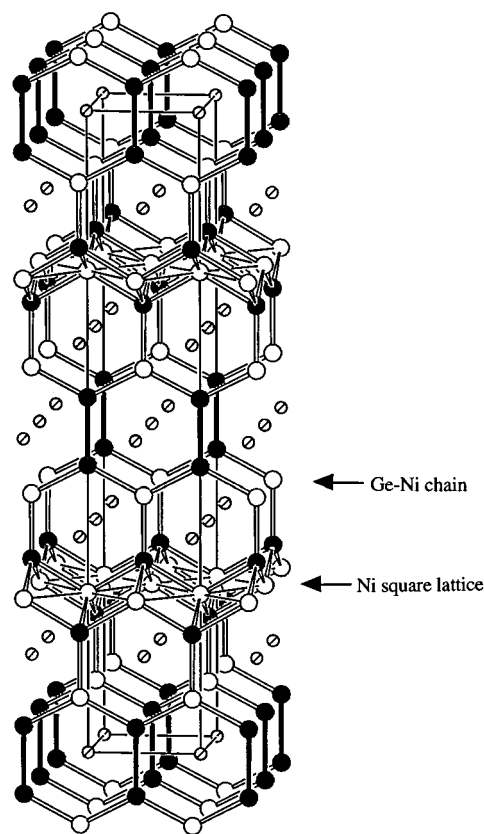


Figure 1. Crystal structure of $\text{La}_3\text{Ni}_4\text{Ge}_4$. It consists of Ge (black circle)-capped Ni (open circle) square lattices and Ge–Ni zigzag chains.

is the subject of our study. Some other related intermetallic compounds are listed in Table 1.

No single-crystal X-ray study has been reported for the LaNiGe_2 structure. According to reported powder data,² it crystallizes in the CeNiGe_2 structure.¹³ But the accurate interatomic distances are unknown. Thus our study includes the synthesis and single-crystal X-ray diffraction study of this compound.

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(1) Witham, C.; Ratnakumar, B. V.; Bowman, R. C., Jr.; Hightower, A.; Fultz, B. *J. Electrochem. Soc.* **1996**, *143*, L205.

(2) Pecharskii, V. K.; Gschneidner, K. A., Jr.; Miller, L. L. *Phys. Rev. B* **1991**, *43*, 10906.

(3) Wernick, J. H.; Hull, G. W.; Geballe, T. H.; Bernardini, J. E.; Waszczak, J. V. *Mater. Lett.* **1982**, *1*, 71.

(4) Venturini, G.; Malaman, B. *J. Alloys. Compd.* **1996**, *235*, 201.

(5) François, M.; Venturini, G.; Malaman, B.; Roques, B. *J. Less-Common Met.* **1990**, *160*, 197.

(6) Pecharskii, V. K.; Mruz, O. Y.; Konyk, M. B.; Salamakha, P. S.; Starodub, P. K.; Fedyna, M. F.; Bodak, O. I. *Zh. Strukt. Khim.* **1989**, *30*, 96.

(7) Bruskov, V. A.; Bodak, O. I.; Pecharskii, V. K. *Izv. Akad. Nauk SSSR Neor. Mater.* **1986**, *22*, 1573.

(8) Pecharskii, V. K.; Bodak, O. I.; Bruskov, V. A. *Kritallografiya* **1986**, *31*, 312.

(9) Bruskov, V. A.; Pecharskii, V. K.; Bodak, O. I. *Kritallografiya* **1984**, *29*, 1071.

(10) Bodak, O. I.; Bruskov, V. A.; Pecharskii, V. K. *Kritallografiya* **1982**, *27*, 896.

(11) Mendelsohn, M. H.; Gruen, D. M. *Rare Earths Mod. Sci. Technol.* **1980**, *2*, 593.

(12) Just, G.; Paufler, P. *J. Alloys Compd.* **1996**, *232*, 1.

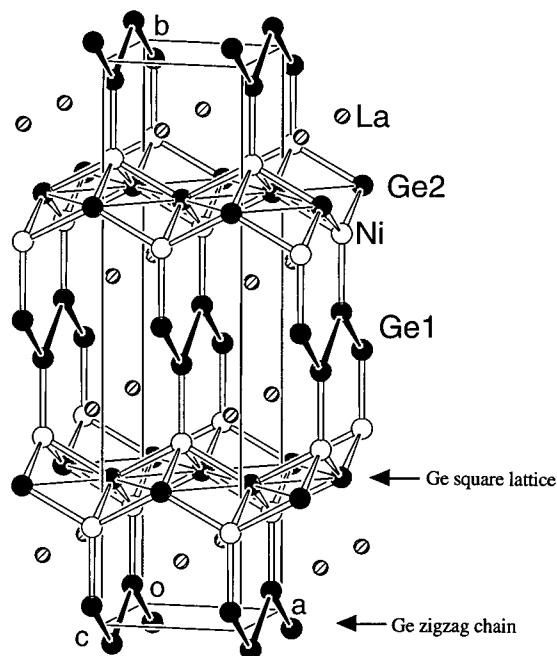


Figure 2. Crystal structure of LaNiGe₂. It consists of Ni (open circle)-capped Ge (Ge2, black circle) square lattices and Ge (Ge1, black circle) zigzag chains.

Table 1. Selected Compounds with a Si, Ge, Fe, or Ni Square Lattice

compound	related structure type	square lattice formed by	capping element	zigzag chain	ref
CeNiSi ₂	CeNiSi ₂	Si	Ni	Si	13
Ce ₃ Ni ₂ Si ₈	CeNiSi ₂	Si	Ni, Si	Si	30
NdRuSi ₂	CeNiSi ₂	Si	Ru	Si	31
TmLi _{0.5} Ge ₂	CeNiSi ₂	Ge	Li	Ge	32
Ce ₂ Rh _{1.35} Ge _{4.65}	CeNiSi ₂	Ge	Rh, Ge	Ge	33
TbFeSi ₂	CeNiSi ₂	Fe	Si	Si	34
U ₃ Ni ₄ Si ₄	CeNiSi ₂	Ni	Si	Ni, Si	35
La ₃ Ni ₄ Ge ₄	CeNiSi ₂	Ni	Ge	Ni, Ge	7
ANi ₂ Ge ₂ (A = Ca, Sr)	ThCr ₂ Si ₂	Ni	Ge	none	36
LnNi ₂ Ge ₂ (Ln = Dy, Ho, Er)	ThCr ₂ Si ₂	Ni	Ge	none	37
YNi ₂ Ge ₂	ThCr ₂ Si ₂	Ni	Ge	none	38

Experimental Section

Synthesis. Although previous syntheses have been made by the arc-melting method,² the relatively low melting point of the reactants indicates that conventional high-temperature synthesis should be feasible to allow the growth of single crystals. Our synthesis was carried out by reacting elemental La (Strem, 2N6 chips), Ni (Fisher, 98.4% pure, dust), and Ge (Atomergic, 99.999% pure, -100 mesh) in 1:2:4 molar ratio (total amount: 0.8 g) in a carbon-black-coated quartz ampule. All preparations were carried out inside an Ar-filled glovebox. The ampule was then sealed under a vacuum of 10⁻⁴ Torr. A computer-controlled furnace was used to heat the ampule to 1100 °C in 72 h. The reaction temperature was held at 1100 °C for 96 h before the sample was annealed to room temperature in 96 h.

Single-Crystal X-ray Diffraction. A black cubic crystal (0.048 × 0.048 × 0.048 mm³) of the title compound was selected and mounted on glass fiber. Diffraction data were collected on an Enraf-Nonius CAD4 automated diffractometer, and 25 intense reflections [16° < 2θ < 30°] were centered using graphite-monochromated Mo Kα radiation. Least-squares refinement of their setting angles resulted in the unit-cell

(13) Bodak, O. I.; Gladyshevskii, E. I. *Sov. Phys. Crystallogr.* **1970**, *14*, 859.

Table 2. Crystallographic Data for LaNiGe₂

chemical formula	LaNiGe ₂
a (Å)	4.3040(6)
b (Å)	16.892(10)
c (Å)	4.2367(5)
V (Å ³)	308.02(6)
Z	4
fw	342.80
space group	<i>Cmcm</i> (No. 63)
T (°C)	20
λ (Å)	0.71073
ρ _{calc} (g cm ⁻³)	7.392
μ (mm ⁻¹)	38.605
R indices ^a [F _o > 4σ(F _o)] (199 data)	R1, 0.0250; wR2 0.0629
R indices ^b (all data)	R1, 0.0271; wR2 0.0666

^a R1 = Σ||F_o - |F_c||/Σ|F_o|. ^b wR2 = [Σ(F_o² - F_c²)²/ΣwF_o⁴]^{1/2}. Weighting: w = 1/[σ²(F_o²) + (0.0331P)² + 1.0759P] where P = (F_o² + 2F_c²)/3.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å²) for LaNiGe₂

atom	x	y	z	U(eq) ^a
La	0	0.39154(3)	1/4	0.0041(3)
Ni	0	0.18248(9)	1/4	0.0060(4)
Ge(1)	0	0.04271(7)	1/4	0.0057(4)
Ge(2)	0	0.75005(7)	1/4	0.0063(4)

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

Table 4. Selected Bond Lengths (Å) and Angles (deg) for LaNiGe₂

Ni–Ge(1)	2.361(2)	Ge(1)–Ge(1)	2.5630(14)
Ni–Ge(2)	2 × 2.4055(9), 2 × 2.4360(10)	La–Ni	4 × 3.2683(7)
La–Ge(2)	2 × 3.1949(10), 2 × 3.2160(10)	La–Ge(1)	4 × 3.2175(5)
Ge(1)–Ge(1)–Ge(1)	111.48(9)		
Ni–Ge(2)–Ni	4 × 102.83(3), 124.12(8), 123.44(8)		
Ge(1)–Ni–Ge(2)	2 × 118.28(4), 2 × 117.94(4)		

parameters reported in Table 2 together with other details associated with data collection and refinement. Data were collected using the ω-scan method with a scan interval of 1.0°, within the limits 8° < 2θ < 54° for -5 ≤ h ≤ 5, 0 ≤ k ≤ 21, 0 ≤ l ≤ 5. The diffracted intensities were corrected for Lorentz and polarization effects; no decay was observed. An empirical absorption correction based on ψ-scans was applied to all data (transmission range 0.197–0.266). The structure was solved by direct methods with SIR92¹⁴ and refined by full-matrix least-squares on F_o² using all the 211 independent reflections and 18 parameters (for 338 reflections collected). Anisotropic thermal displacement were assigned to all atoms, and an empirical extinction coefficient, as implemented in SHELX-93,¹⁵ was refined to a value of 0.0096(7), giving a significant improvement in the agreement factors. The final difference electron density map shows no features with a height greater than 5% of a Ge atom. All calculations were performed using SHELX-93.¹⁵ Crystal drawings were produced with SCHAKAL.¹⁶ Final atomic coordinates, average temperature factors, selected bond lengths, and angles are reported in Tables 3 and 4.

Results and Discussion

Structural Description. The LaNiGe₂ structure consists of Ge square lattice layers with Ni capping on

(14) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(15) Sheldrick, G. M. *SHELX-93: program for structure refinement*; University of Goettingen: Germany, 1994.

(16) Keller, E. *SCHAKAL 92: a computer program for the graphical representation of crystallographic models*; University of Freiburg: Germany, 1992.

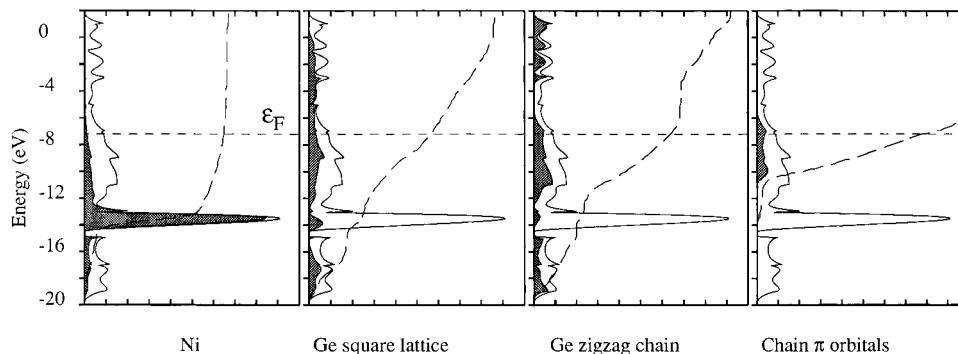


Figure 3. Computed density of states (DOS) of LaNiGe₂. The solid line is total DOS, the shaded area is the individual contribution (from Ni, Ge in the square lattice, Ge in the zigzag chain, and Ge π states, respectively) to the total DOS, and the dashed line is the integrated contribution.

Table 5. Extended Hückel Parameters^{39,40}

	orbital	H_{ii} (eV)	ζ_1^a	ζ_2	c_1^a	c_2
La	6s	-7.67	2.14			
	6p	-5.01	2.08			
	5d	-8.21	3.78	1.381	0.7765	0.4586
Ge	4s	-16.0	2.16			
	4p	-9.0	1.85			
Ni	4s	-9.17	1.83			
	4p	-5.15	1.13			
	3d	-13.49	5.75	2.00	0.5683	0.6292

^a Exponents and coefficients in a double- ζ expansion of the d orbital.

the square hollows and Ge zigzag chains (Figure 2). The Ge–Ge contact in the Ge square lattice is 3.020 Å, much longer than the Ge–Ge distance of 2.45 Å in the elemental, diamond-like Ge structure. Therefore there is very little covalent character in this contact. The Ge–Ge distance in the Ge zigzag chain is 2.563 Å, slightly longer than the Ge–Ge distance in the elemental Ge lattice. The Ge–Ni distance is 2.361 Å, close to the sum of the covalent radii of Ge (1.22 Å) and Ni (1.15 Å), and there is obviously covalent character in this contact. The Ge zigzag chain formation has been seen in other solids such as DyGe₃,¹⁷ whose electronic structure has been analyzed in detail by Albert, Meyer, and Hoffmann.¹⁸ In DyGe₃, the Ge–Ge distance in the chain is 2.505 Å, comparable to the distance in LaNiGe₂. The formation of the Ge square lattice is unique, since in many other related structures it is the transition metal that forms the square lattice (Table 1). However, the Ge square lattice is known in several other structures such as the CaBe₂Ge₂ lattice¹⁹ which is a variation of the populous ThCr₂Si₂ structure.¹² Computational studies showed that the formation of the Ge square lattice is facilitated by the interlayer donor–acceptor interaction common in discrete inorganic complexes.²⁰

Computational Analysis of Electronic Structure.

The density of states (DOS) and crystal orbital overlap populations (COOP) were computed with the extended Hückel tight-binding method.^{21–23} A set of 125 special

k-points in the irreducible wedge of the Brillouin zone of the reciprocal lattice was used in the computation.²⁴ The extended Hückel parameters are listed in Table 5. The computation with all atoms showed that most of the La states are above the Fermi level, a feature that is consistent with the notation that La acts primarily as an electron donor, and the interaction with La is mainly ionic. However, because of the many empty d orbitals of La and the nature of the Mulliken population analysis which is based on the coefficients of the interacting orbitals, La was assigned an unrealistic charge of La^{0.4+}. Therefore the subsequent computations were carried out without the La atoms. The final relative energetic results are the same as those with the La atoms, but the calculated atomic charges are more realistic. The computed DOS is shown in Figure 3. The Ni states are localized around -13.5 eV, while the Ge states spread out widely. However, there is a small difference in the Ge states. The Ge state in the square lattice is slightly more dispersed, as approximately 55% of it is below the Fermi level. The Ge state in the zigzag chain has about 63% below the Fermi level. Thus Ge in the zigzag chain accumulates more electron density. At the extended Hückel level, the Ge atoms in the zigzag chain are more negative (Ge^{1.0-}) than the Ge atoms in the square lattice (Ge^{0.4-}).

According to the calculated band structure (not shown here), the molecular orbital interaction can be constructed readily. It is similar to that of another germanium compound, BaZn₂Ge₂, that we have studied.²⁵ A formal electron partition of La³⁺(Ni³⁻)Ge₂ gives a framework of Ni³⁻Ge'Ge'', where Ni is at the capping site (see Figure 2), Ge' is in the zigzag chain (Ge1 site in Figure 2), and Ge'' is at the square lattice site (Ge2 site in Figure 2). For every hollow in the Ge'' square lattice, a Ge'' atom at the corner of the square contributes an sp³ hybrid. The four sp³ hybrids at a square hollow form symmetry-adapted, cyclobutadienoid molecular orbitals. The a₁ and e orbitals interact with an sp hybrid (hy_{in}) and p_x, p_y orbitals of the capping Ni as they match symmetry patterns. Notice that we ignore the filled d block of Ni for simplicity. The b₂ orbital has no interacting partner of matching symmetry from the capping Ni; it is mainly nonbonding. The result is that

(17) Schobinger-Papamantellos, P.; de Mooij, D. B.; Buschow, K. H. J. *J. Alloys Compd.* **1992**, *183*, 181.

(18) Albert, K.; Meyer, H.-J.; Hoffmann, R. *J. Solid State Chem.* **1993**, *106*, 201.

(19) Eisenmann, B.; May, N.; Müller, W.; Schäfer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1972**, *27*, 1155.

(20) Zheng, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 3078.

(21) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(22) Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London* **1979**, *A366*, 23.

(23) Wijeyesekera, S. D.; Hoffmann, R. *Organometallics* **1984**, *3*, 949.

(24) Pack, J. D.; Monkhorst, H. J. *Phys. Rev. B* **1977**, *16*, 1748.

(25) Proserpio, D. M.; Artioli, G.; Mulley, S.; Chacon, G.; Zheng, C. *Chem. Mater.* **1997**, *9*, 1463.

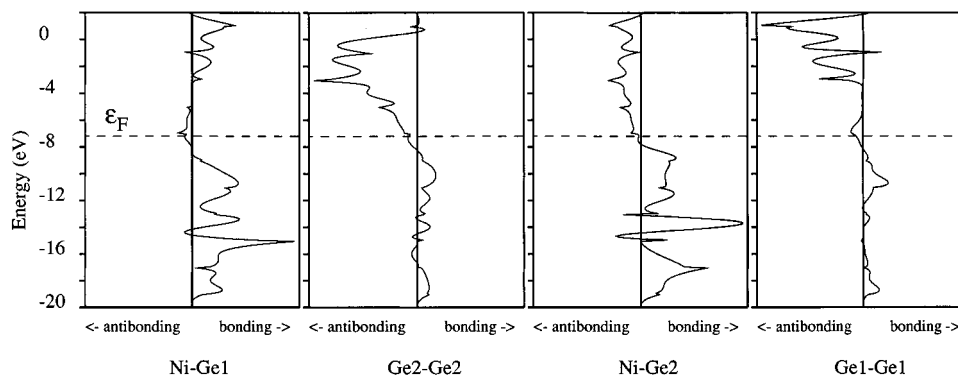
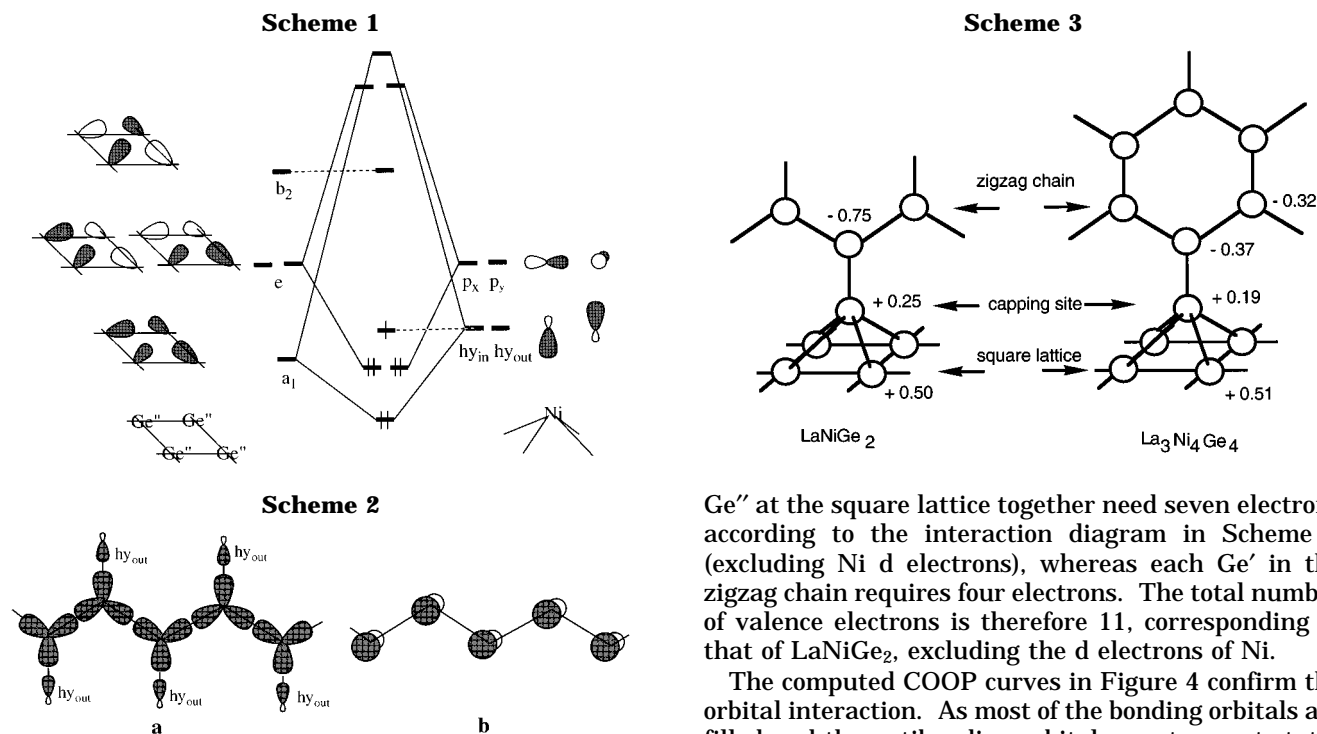


Figure 4. Crystal orbital overlap population (COOP) curves for the layer–chain Ni–Ge bond, Ge–Ge contact within the Ge square lattice, Ni–Ge bond in the NiGe₅ pyramid, and the Ge–Ge bond in the Ge zigzag chain of LaNiGe₂.



three bonding molecular orbitals are formed capable of accommodating six electrons. A seventh electron can occupy the nonbonding orbital of another sp hybrid (hy_{out}) of the capping Ni. Thus for a NiGe₄ pyramid (corresponding actually to one Ge atom since each Ge'' at a corner contributes only one of its four sp^3 hybrids), a suitable electron count is seven excluding the Ni d electrons. The interaction diagram is shown in Scheme 1.

The interaction between the NiGe₄ pyramid and the Ge' zigzag chain is through the second sp hybrid (hy_{out}) of the capping Ni. Each Ge' in the zigzag chain forms three sp^2 hybrids, two of them used to form σ bonds with adjacent Ge' atoms, one used to form a σ bond with the hybrid (hy_{out}) of the capping Ni (Scheme 2a). The p_z orbitals perpendicular to the plane of the zigzag chain form conjugated π orbitals shown in Scheme 2b. Thus the electronic structure of the zigzag chain is similar to that of a polyacetylene polymer. Much of the charge on the zigzag chain of Ge' is in the π orbitals (see Figure 3). In fact, 76% of the π band is below the Fermi level, indicating that 26% of the π^* state is occupied.

The overall electronic structure can be obtained by combining Schemes 1 and 2. Ni at the capping site and

Ge'' at the square lattice together need seven electrons according to the interaction diagram in Scheme 1 (excluding Ni d electrons), whereas each Ge' in the zigzag chain requires four electrons. The total number of valence electrons is therefore 11, corresponding to that of LaNiGe₂, excluding the d electrons of Ni.

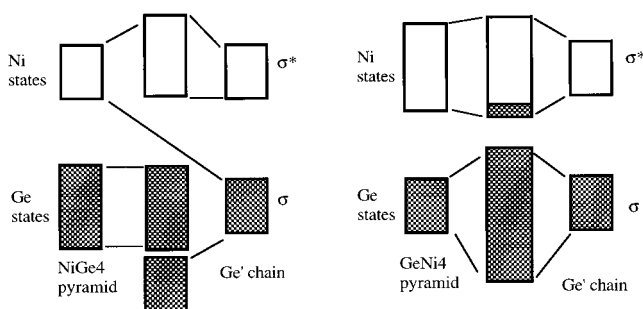
The computed COOP curves in Figure 4 confirm the orbital interaction. As most of the bonding orbitals are filled and the antibonding orbitals empty, most states below the Fermi level all contribute to bonding, while those above the Fermi level contribute to antibonding for the bonds in the square lattice, zigzag chain, and between them. There are some antibonding states below the Fermi level, in particular, that of the π^* state which is shown in Figure 3. Since the DOS at the Fermi level is nonzero, the compound should be metallic, as a heat capacity measurement indicated such.²

Donor Layer–Acceptor Chain Formation. As discussed previously,²⁵ the Ge square lattice has larger band dispersion and thus acts as an electron donor. The larger band dispersion results in a repulsive interaction that it is energetically unfavorable.²⁶ The question is why such a square lattice of more electronegative atoms exists in intermetallic compounds.

To understand this phenomenon, we computed the charge distribution for hypothetical, all Ge, neutral frameworks of both the LaNiGe₂ and La₃Ni₄Ge₄ lattices. The charge distribution is shown in Scheme 3. It can be seen from this scheme that positive charge accumulates at the square lattice and the capping sites.

(26) Albright, T. A.; Burdett, J. K.; Whangbo, M. *Orbital interactions in chemistry*; Wiley: New York, 1985.

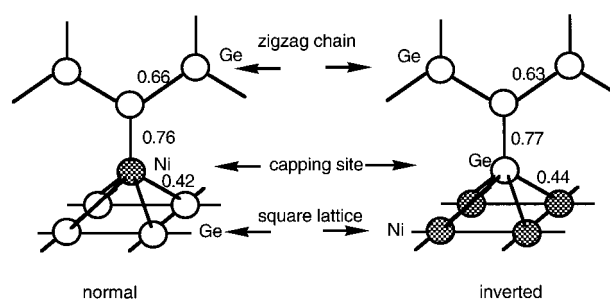
Scheme 4



The square lattice site is most positive. Thus, according to a substitution rule,²⁷ the most electropositive element should reside at the square lattice site. This is indeed the case for the La₃Ni₄Ge₄ lattice, where Ni occupies the square lattice site.

For the LaNiGe₂ lattice, the situation is different. If Ni takes the square lattice site, Ge will occupy the capping site. Then there will be a covalent interaction between the capping Ge and Ge' in the zigzag chain. This interaction will push some of the Ge'–Ge' bonding states in the Ge' chain above the Fermi level, resulting in the weakening of the Ge'–Ge' bonds. On the other hand, if the more electronegative atom, Ge, resides in the square lattice, the capping Ni will interact with the Ge zigzag chain in a donor–acceptor pattern. The states that will be pushed above the Fermi level are mostly Ni empty states. The Ge'–Ge' bond is therefore affected less. Thus the unfavorable band dispersion is compensated by the interlayer donor–acceptor interaction. The orbital interaction for the two possible arrangements is schematically shown in Scheme 4. On the left side of Scheme 4 is the interaction pattern for the structure in which a square lattice is formed by the more electronegative atoms (Ge). The lower, occupied square lattice state (occupied states are shaded) has larger band dispersion, but it interacts with the Ge' zigzag chain through the top of the NiGe₅ pyramid, where it is mostly a Ni unoccupied state (excluding the filled d shell). The layer–chain interaction is that of the Dewar–Chatt–Duncanson donation–back-donation type,^{28,29} similar to that of another class of compounds of the CaBe₂Ge₂ type, where the more electronegative

Scheme 5



Ge also forms a square lattice.¹⁹ On the right side of Scheme 4 is the interaction pattern for a structure in which the square lattice is occupied by the more electropositive element (Ni) and thus has a larger band dispersion in the upper, unoccupied state. The lower, occupied state of the Ge atoms in the capping site (top of the GeNi₅ pyramid) interacts with the Ge' states in the zigzag chain. This interaction will push some of the Ge'–Ge' bonding states above the Fermi level ϵ_F .

Scheme 5 shows the computed overlap populations for the normal (actual crystal structure) and the inverted LaNiGe₂ lattice. Indeed, in the normal lattice, the capping Ni–square lattice Ge bond is weaker due to the band dispersion mentioned above, but the Ge'–Ge' bonds in the zigzag chain are stronger than that in the inverted lattice. The computed difference at the inverted Hückel level is small, and the balance of these two types of interactions, within the layer and between the layer and the zigzag chain, is very subtle. The computed energy favors the normal structure by 0.17 eV per unit cell. For the La₃Ni₄Ge₄ lattice, however, the computation favors the structure with the square lattice of Ni (actual structure) over the inverted one (Ge square lattice) by 4.4 eV per unit cell. It should be noted that if the d block is not filled in the LaNiGe₂ structure, d orbitals will participate in the interaction to favor the pattern on the right side of Scheme 4. An example is TbFeSi₂ (see Table 1), where Fe forms the square lattice.

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Supporting Information Available: Full list of data collection parameters, structure refinement details, atomic coordinates, and anisotropic displacement parameters (7 pages); table of structure factors (2 pages). Ordering information is given on any current masthead page.

CM9706210

(27) Burdett, J. K. *Chemical Bonding in Solids, Section 8.6*; Oxford University Press: New York, 1995.

(28) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, 18, C71.

(29) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

(30) Stepien, J. A.; Lukaszewicz, K.; Gladyshevskii, E. I.; Bodak, O. I. *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **1972**, 20, 1029.

(31) Cenxual, K.; Gladyshevskii, R. E.; Parthe, E. *Acta Crystallogr. Sect. C* **1992**, 48, 225.

(32) Pavlyuk, V. V.; Bodak, O. I.; Sobolev, A. N. *Sov. Phys. Crystallogr.* **1991**, 36, 493.

(33) Shapiey, B. I.; Sologub, O. L.; Seropegin, Y. D.; Bodak, O. I.; Salamakha, P. S. *J. Less-Common Met.* **1991**, 175, L1.

(34) Yarovets, V. I.; Gorelenko, Y. K. *Visn. L'viv Derzh. Univ. Ser. Khim* **1981**, 23, 20.

(35) Yarmolyuk, Y. P.; Akselrud, L. G.; Grin, Y. N.; Fundamenskii, V. S.; Gladyshevskii, E. I. *Sov. Phys. Crystallogr.* **1979**, 24, 332.

(36) Dörrscheidt, W.; Niess, N.; Schäfer, H. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, 31, 890.

(37) Andre, G.; Bonville, P.; Bouree, F.; Bombik, A.; Kolenda, M.; Oles, A.; Pacyna, A.; Sikora, W.; Szytula, A. *J. Alloys Compd.* **1995**, 224, 253.

(38) Bel'skil, V. K.; Bodak, O. I.; Gladyshevskii, E. I.; Zavodnik, V. E.; Pecharskil, V. K. *Doklady Akademii Nauk SSSR* **1986**, 291, 1362.

(39) Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* **1978**, 17, 126.

(40) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. J. *Am. Chem. Soc.* **1976**, 98, 3219.