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$V_2Al_5Ge_5$: first ternary intermetallic in the V–Al–Ge system accessible in liquid aluminium†

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The intermetallic compound $V_2Al_5Ge_5$ grown from Al flux is reported. $V_2Al_5Ge_5$: orthorhombic, *Cmcm*, $a = 5.4072(10)$, $b = 12.978(2)$, and $c = 11.362(2)$ Å, the structure features distorted pentagonal prismatic columns defined by Al and Ge atoms. Vanadium atoms occupy the central axis of columns forming a chain with long–short alternation of V–V bonds. This compound is resistant to air oxidation up to 500 °C.

Exploratory synthesis in a molten metal medium has shown great promise in the field of intermetallic compounds.[1,2,3] Not only can flux growth lower the reaction temperature, it can facilitate the growth of large single crystals, which makes characterization and physical properties measurements more reliable.[4] Recently, we suggested using liquid Al as a solvent to synthesize new intermetallics including silicides and germanides, for example, $RENiAl_4Ge_2$,[5] $RE_4Fe_{2+x}Al_{7-x}Si_8$,[6] and $REAu_3Al_7$.[7] The systems explored to date typically consist of a rare earth metal RE, a transition metal, aluminium and silicon or germanium. Also of interest are systems without rare earth elements, containing only a transition metal and germanium, which have not been studied systematically or extensively and they are relevant in the field of advanced aluminium alloys. Past exploration of the V–Al–Ge system using high temperature direct combination reactions yielded only two pseudo-binary phases $V_3Al_{(1-x)}Ge_x$ and $V_3Ge_{(1-x)}Al_x$ which belong to the A15 structure type.[8] Here we describe the first ternary germanide $V_2Al_5Ge_5$ presenting a new structure type, formed under the relatively mild synthetic conditions from the reaction of vanadium and germanium in molten aluminium.‡

The compound $V_2Al_5Ge_5$ was obtained from liquid Al in the form of elongated needles, frequently aggregated in bundles. It crystallizes in the space group *Cmcm* (#63)§ in what appears to be a new structure type (Fig. 1). In this structure a total of seven crystallographically distinct atomic sites were identified: V atoms at 8*g* sites, and Al and Ge atoms occupying three atomic sites: two at 8*f* and one at 4*c*. A recognizable building block in the structure is a distorted pentagonal prismatic column made of stacked pentagonal prisms defined by Al and Ge atoms. Each prism has a V atom in the center (Fig. 2A). The pentagonal prisms have been seen in other compounds such as CeGaMg, in which Ga and Mg atoms build a three dimensional network with Ce atoms filling in the pentagonal channels.[9] In $V_2Al_5Ge_5$ the pentagonal prism is not regular: one of its pentagonal faces contains one Al(1) atom, two symmetry-related Al(3) atoms and two symmetry-related Ge(2) atoms, while on the opposite face, correspondingly, there are one Ge(1) atom, two Ge(3) atoms and two Al(2) atoms. The pentagonal prisms stack along the *a* axis to make a column by sharing the top and bottom faces with two other prisms. Therefore each V atom is not only surrounded by five Al atoms and five Ge atoms, but also bonded with two V atoms inside the column forming a vanadium atom chain (see Fig. 2A), which is rarely seen in other vanadium-containing intermetallic compounds.[10] Another interesting feature of this structure is long–short alternation of the V–V bond distances in the chain at 2.732(2) Å and 2.676(2) Å, respectively. Both distances imply V–V bonding and are comparable to those found in other intermetallic compounds such as AlV_3 and V_4Al_{23}.[11] The difference in bond distance indicates that the V atom is not located exactly at the center of the prism. In fact, the V atom is closer to the face with two Ge atoms and three Al atoms (plane Al(1)–Al(3)–Ge(2), Fig. 2A). To show the structural organization of $V_2Al_5Ge_5$ more clearly, all Al atoms were removed (Fig. 1B). The whole

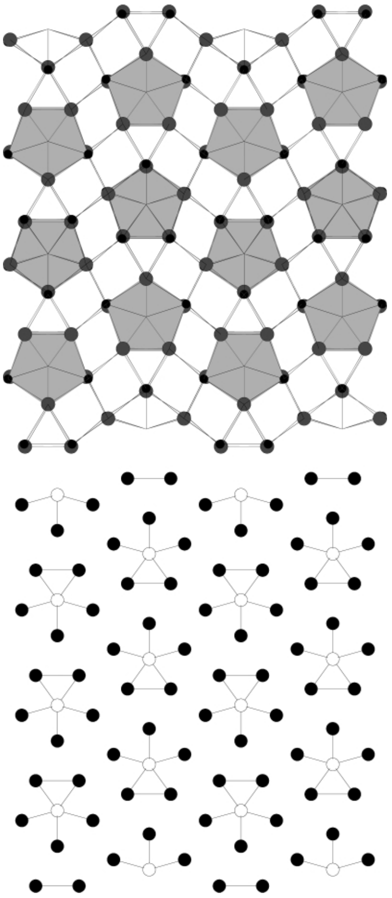

Fig. 1 Structure of $V_2Al_5Ge_5$ (top) viewed down the *a* axis highlighting pentagonal columns. (Bottom) Al atoms removed for clarity to show identical "V_2Ge_5" column running, down the *a* axis.

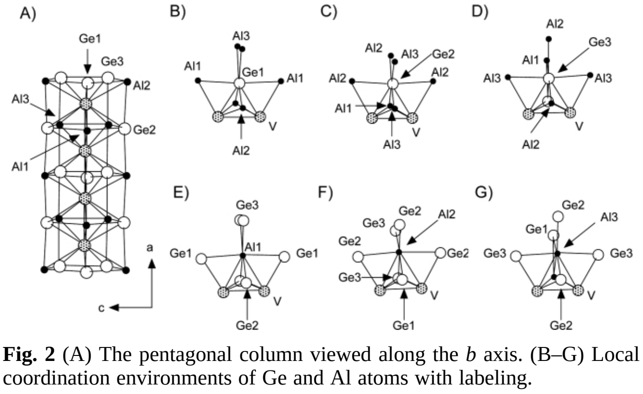

Fig. 2 (A) The pentagonal column viewed along the *b* axis. (B–G) Local coordination environments of Ge and Al atoms with labeling.

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† Electronic supplementary information (ESI) available: structure of $V_2Al_5Ge_5$. See http://www.rsc.org/suppdata/cc/b4/b404035j/

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structure can be described as hexagonally close-packed pentagonal columns parallel to the *a* axis.

The local coordination environments of Al and Ge atoms within 3.0 Å are presented in Fig. 2B–G. Each Ge atom is surrounded by eight atoms, and they exhibit similar coordination geometry. The Ge(1) atom is sitting at the cross-section of two planes: one plane is defined by atoms Al(1)–V–V–Al(1), the other plane is perpendicular and defined by atoms Al(2)–Al(3)–Al(3)–Al(2). Ge(1), Al(2) and V atoms are connected to form a triangular pyramid. The Ge(2) atom shows a similar geometry as Ge(1), but in this case, the two Al(3) atoms are from different pentagonal clusters, so there is no bonding between them, as shown in Fig. 2C. Another noteworthy point is that the two triangles Al(2)–V–Ge(2) connected by the Ge(2) atom are not co-planar as described in Fig. 2C. Ge(3) atom also presents a similar coordination environment, but it is different from those of Ge(1) and Ge(2) atoms, particularly in the triangular pyramid. One of the Al atoms in the apex positions is displaced by one Ge(3) atom, with Ge(3)–Ge(3) bond distance of 2.6791(15) Å. The Al atoms show very similar coordination geometries to the Ge atoms (shown in Fig. 2E–G) and we will not discuss them here in detail.

Electronic structure calculations using linearized augmented plane wave method within density functional theory¶ show metallic behavior of $V_2Al_5Ge_5$ with a density of states of about 8 states eV^{-1} $(2[V_2Al_5Ge_5])^{-1}$ (Fig. 3A). The Ge p states in the energy range -7 to 10 eV hybridize with the Al p and Al s states indicating the covalent interaction between Ge and Al atoms (Fig. 3B–C). The V d states are partially occupied (Fig. 3D). The occupied states in the range -4 to -0 eV hybridize more with Ge p states than Al p and Al s states, suggesting a stronger covalent interaction between V and Ge than V and Al. Magnetic susceptibility measurements indicate Pauli paramagnetism for the compound, which is consistent with the predicted metallic behavior discussed above.

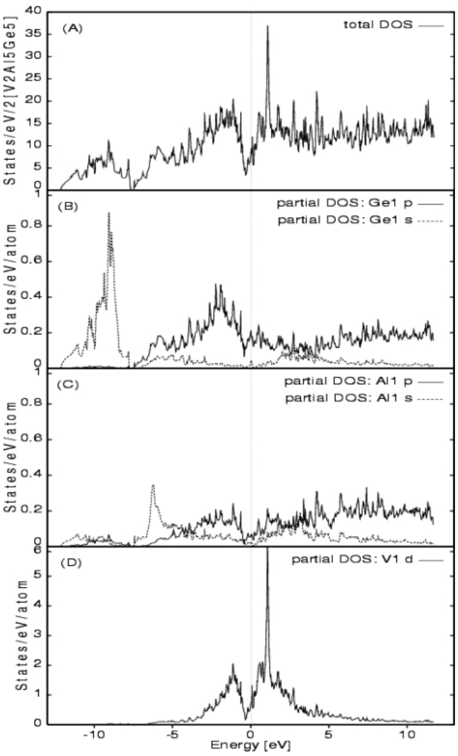

Fig. 3 Density of states for $V_2Al_5Ge_5$. The Fermi level is at 0 eV.

An interesting property of $V_2Al_5Ge_5$ is its resistance to air oxidation up to 500 °C. Crystals of the compound were exposed to air in a thermal gravimetric furnace environment. No weight gain or loss was observed up to ~ 520 °C. Above this temperature however a continuous weight gain which continues up to 1000 °C was observed. The oxidation is complete leading finally to the oxides.

Al flux is a powerful solvent to synthesize and explore new intermetallic compounds. The $V_2Al_5Ge_5$ phase is such an example and apparently the first ternary member in the V–Al–Ge system. The pentagonal columnar building block of the structure and the one-dimensional V–V bonding running along the central axis of the columns are salient features of this structural motif.

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Notes and references

‡ $V_2Al_5Ge_5$ was obtained by combining vanadium (0.102 g, 0.002 mol) and germanium (0.36 g, 0.005 mol) in excess aluminium (0.405 g, 0.015 mol). The sample was loaded into an alumina tube, which was then sealed in a quartz tube under vacuum (~ 10^{-4} Torr). The starting reagents were heated up to 850 °C, maintained at this temperature for 3 days, slowly cooled down to 200 °C at the rate of 15 °C h^{-1}, and finally brought down to 50 °C in 5 h. The excess Al was removed with 5 M aqueous NaOH solution, and the product was washed with water and acetone (~ 90% yield based on V). The crystals are stable in the air. Pure material can also be obtained quantitatively by heating V, Al and Ge in a stoichiometric ratio using the same heating profile.

§ A Siemens SMART platform CCD diffractometer was used to collect data from a crystal of $0.22 \times 0.17 \times 0.15$ mm^3 dimensions and Mo Kα (λ = 0.71073 Å) radiation. An empirical absorption correction was applied to the data using SADABS. Crystal data: $V_2Al_5Ge_5$, orthorhombic, *Cmcm* (#63), a = 5.4072(10) Å, b = 12.978(2) Å, c = 11.362(2) Å, V = 797.4(3) $Å^3$, Z = 4, D_c = 4.996 g cm^{-3}, μ = 21.293 mm^{-1}; index range $-9 < h < 9$, $-22 < k < 22$, $-19 < l < 19$; total reflections 6346, independent reflections 1133 (R_{int} = 9.65), and 40 parameters; $R1$ = 4.86, $wR2$ = 8.95, GOF = 1.064. CCDC 234454. See http://www.rsc.org/suppdata/cc/b4/b404035j/ for crystallographic data in .cif or other electronic format.

¶ Band structure calculations were performed using the self-consistent full-potential linearized augmented plane wave method (LAPW) within density functional theory (DFT) using the generalized gradient approximation (GGA) for the exchange and correlation potential. Scalar relativistic corrections were added and spin–orbit interaction (SOI) was incorporated using a second variational procedure. The calculations were performed using the WIEN97 program.

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