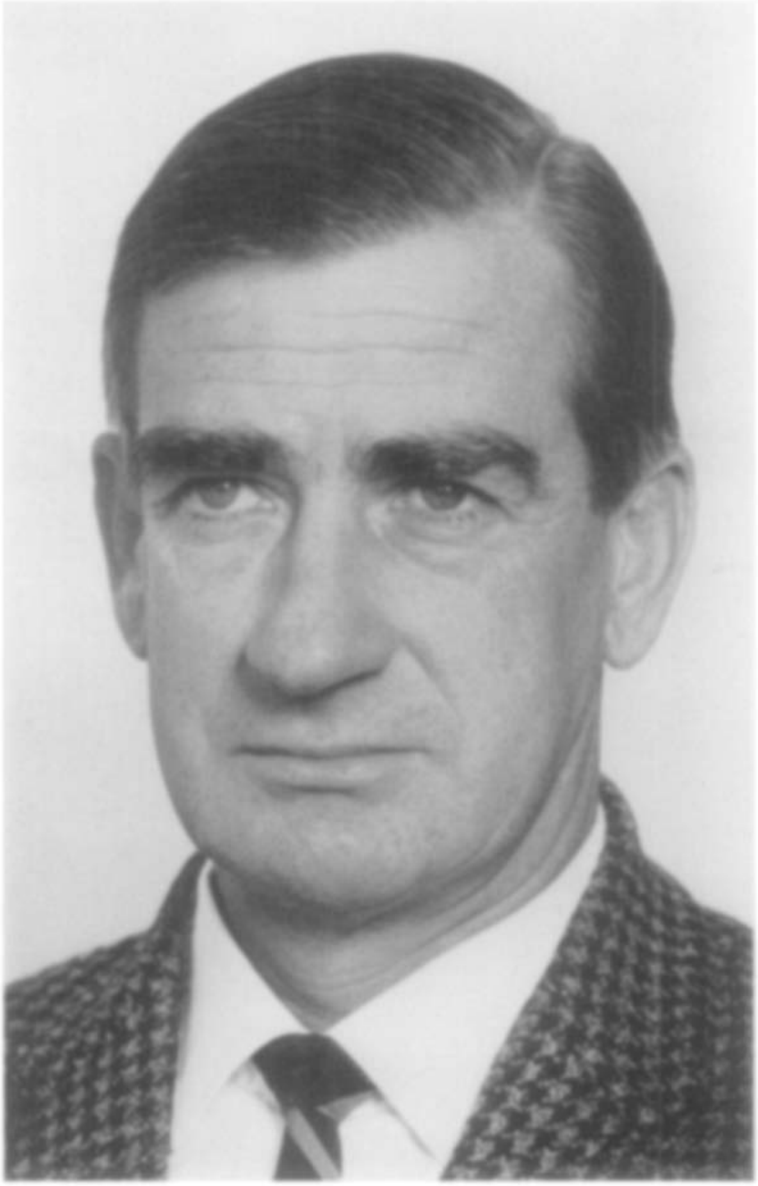

Arthur David Wadsley
1918 – 1969

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By the death of David Wadsley on 6 January 1969 inorganic chemistry has lost one of its great men. Wadsley had deeply penetrated the most difficult problems in oxide chemistry with his mastery of methods, skill and imagination. He was in the middle of an unusually successful career, Head of the Inorganic Chemistry Section and Assistant Chief of the Division of Mineral Chemistry of CSIRO in Melbourne.

Wadsley was born in Hobart, Tasmania. After his M.Sc. at the University of Tasmania, he joined in 1943 the CSIRO Division of Industrial Chemistry. Wadsley's first crystal structure work, which gave him his Doctorate of Science from the University of Tasmania in 1956, dealt with manganese oxides. After having worked out the structures of lithiophorite $(Al,Li)MnO_2(OH)_2$, psilomelane $(Ba,H_2O)_2Mn_5O_{10}$ and chalcophanite $ZnMn_3O_7{\cdot}3H_2O$ and the bronze $Na_{2-x}V_6O_{15}$, he wrote in 1954 the brilliant review article "The crystal chemistry of non-stoichiometric compounds," *Rev. Pure Appl. Chem.* 5, 165 (1955). In this article we find for the first time the now well-known concepts of block and shear structures. Shortly afterwards the structure of another important vanadium bronze, $Li_{1+x}V_3O_8$, was published.

Wadsley maintained his great interest in oxide bronzes through the years. The first bronze with dioxide composition, $Na_xTi_4O_8$, was synthesized and its structure determined during 1960. The molybdenum bronzes had been prepared by A. Wold and his group in USA 1964 and their complicated crystal structures were solved by Wadsley in cooperation with N. C. Stephenson and J. Graham.

Wadsley's work on niobium oxide chemistry started with the crystal structure determinations of the shear compounds $TiNb_2O_7$ and $Ti_2Nb_{10}O_{29}$. With these two structures—so often used by Wadsley and others to illustrate the crystallographic shear concept and the block principle—and with the alkalititanates $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$, the idea of intergrowth in solids had started to emerge.

In a new review article, "Inorganic Non-stoichiometric Compounds," in "Non-stoichiometric Compounds," (L. Mandelcorn, Ed.), p. 161, Academic Press, Inc., New York, 1964, Wadsley critically examined current theories in solid state chemistry. He summarized experimental work and crystal structures and pointed out, as he had done so often earlier, that wide ranges of homogeneity, attributed to vacancies or interstitials or other defects, had to be rejected in a number of oxide systems. He classified non-stoichiometric compounds in a new way, and indicated again the importance of shear compounds, and the possibility of shear planes as planar faults.

When making phase studies between $Ti_2Nb_{10}O_{29}$ and Nb_2O_5, Wadsley observed that the material "gave a bewildering variety of diffraction patterns, bearing considerable similarities to one another as well as to α-Nb_2O_5." He decided to solve the structure of α-Nb_2O_5 ($\equiv$H–Nb_2O_5). The Nb_2O_5 problem had for more than a decade defied oxide crystallographers all over the world. Several modifications were known, but none of their structures. Wadsley and B. M. Gatehouse, also from Tasmania, solved the H–Nb_2O_5 structure during the autumn 1962. This was a clue indeed. A dynamic development started and up to now about thirty compounds have been made with different and new structures, all related to and derived from the crystal structure of H–Nb_2O_5. Some of them have very complex composition ($Nb_{59}O_{147}F$ may serve as an example) but nevertheless simple structural relationships to H–Nb_2O_5 always exist.

R. S. Roth, on leave from NBS, USA, came to Melbourne in 1964 for one year with Wadsley. He brought the compounds $TiNb_{24}O_{62}$ and PNb_9O_{25}, and with their knowledge of the H–Nb_2O_5 structure, they were easily able to solve these structures. The building block principles were then outlined from these two compounds and a number of compounds they found in the Nb_2O_5-WO_3 system ($WNb_{12}O_{33}$, $W_3Nb_{14}O_{44}$, $W_5Nb_{16}O_{55}$ and $W_8Nb_{18}O_{69}$), all related to H–Nb_2O_5. What earlier had been described as solid solutions in the systems TiO_2–Nb_2O_5 and Nb_2O_5–WO_3, had instead been found to consist of a number of compounds. The old question was again raised. If there is a solid solution of WO_3 or TiO_2 in Nb_2O_5, or if each of the new compounds found had a range of existence, what would the mechanism be? Wadsley's thought was invariably that blocks of different sizes, joined by intergrowth, was the explanation. At this time R. Gruehn in Professor H. Schäfer's group in Münster, had prepared with careful technique another Nb/W oxide, $W_4Nb_{26}O_{77}$. With material from Münster, Wadsley and coworkers found that this compound contained two different sizes of blocks, and that it was an ordered intergrowth between $WNb_{12}O_{33}$ and $W_3Nb_{14}O_{44}$. Another pressing question concerned the mobility of shear planes, or in other words, could the block size be changed by diffusion? Through geometrical and simple chemical considerations this was shown to be the case and published in 1966. Wadsley now looked for a suitable method which would provide him with the experimental evidence. Together with J. G. Allpress and J. V. Sanders he examined the mixed Nb/W oxides by electron microscopy and electron diffraction. Lattice images were generated and planar faults were observed in the structures. The faults corresponded to shear planes representing the partial intergrowth of one phase with another. The faults could be as small as half a unit cell in width—a single fault, or larger, consisting of several unit cells of the second phase. The composition of these nonperiodic blocks differs from that of the host lattice. This work confirmed what Wadsley had proposed and propagated during many years. There are strong reasons to expect that nonperiodic shear structures are common for the majority of the transition metal oxide systems. This is the proper occasion to suggest—as a distinction for a scientist of unusual originality—to name this discovery *Wadsley intergrowth defects.*

The alkali titanate work was continued by Wadsley with W. G. Mumme and A. F. Reid, and resulted in several important papers. $NaTi_2Al_5O_{12}$ was synthesized and its structure, with a new arrangement of joining tetrahedra and octahedra, indicates that a great deal of attention will be paid to it. $Na_2Ti_7O_{15}$ is another ordered intergrowth compound in its structure between $Na_2Ti_6O_{13}$ and "$Na_2Ti_8O_{17}$."

Wadsley started crystal structure work with such manganese minerals as psilomelane and hollandite. I recall from discussions as early as 1960 his opinion that the felspar sanidine, $KAlSi_3O_8$, could transform under high pressure into the hollandite structure. His general thought was that the tetrahedral silicate chemistry could transform into octahedral silicate chemistry, and it would then be very similar to the manganese and titanium oxide chemistry. A few years ago he started with A. F. Reid and A. E. Ringwood a study of silicate systems under high pressure, in order to increase the knowledge of the phase relations at depths between 200–900 km in the earth's mantle. They showed that sanidine, $KAlSi_3O_8$, indeed transforms into the hollandite structure. They also found that $NaAlGeO_4$, a model substance for nepheline, $NaAlSiO_4$, transforms at high pressure to a calcium ferrite isotype and they could predict the density for such a high-pressure form of nepheline.

Their contribution to the olivine-spinel transformation is typical of Wadsley. This transformation leads to a density increase of approximately 10%. Mn_2GeO_4, a model substance for olivine, was compressed and found to transform into a new phase, which was not of spinel type with mixed octahedra and tetrahedra, but with both the metals in sixfold coordination. The density increase was 17.3%.

Without hesitation Wadsley successfully tackled the most important problems in inorganic chemistry and at the time they were the most difficult ones; he was a courageous man. The present understanding of nonstoichiometry largely stems from his work in which crystallography was the tool he used as a chemist. In all respects, he tried to predict what would happen when a solid reacted or was transformed. A scientific discussion was a challenge to him; he seemed to have an immense supply of ideas, predictions or explanations to unexplained phenomena or unexplored fields. He was a very colourful personality. In his work Wadsley was careful and exact. The rapid development in solid state chemistry during the last several years clearly shows that he was a person with a grip on chemistry and down-to-earthness that was very impressive. He was indeed guided by the intuition that comes from profound knowledge and experience, skill, and intelligence.

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