

one. Seules les longueurs C(8)–C(9) et C(8)–C(12) sont significativement plus courtes dans le cas présent (1,46 et 1,44 Å au lieu de 1,49 et 1,50), sous l'influence d'un effet de conjugaison avec la liaison double adjacente C(8)–C(7). La 3-méthyl-4-benzal-isoxazoline-5-one est une molécule plane: l'angle entre les plans moyens des atomes 1 à 6, d'une part, et 7 à 12 d'autre part, vaut 1°. Cette planéarité entraîne l'ouverture de certains angles de valence:

C(6)–C(1)–C(7)	126°
C(1)–C(7)–C(8)	132
C(7)–C(8)–C(9)	134
C(8)–C(9)–O(13)	133;

la distance O(13)–H(19) restant néanmoins très courte (2,10 Å).

La Fig. 3 montre la disposition des molécules dans la maille.

Les principaux contacts intermoléculaires sont:

N(11)···H(17) ($\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$)	2,66 Å	
et		
O(10)···C(14)	} (x, 1 + y, z)	
O(13)···H(20)		3,30
O(13)···H(15)		2,55
	2,60	

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X-ray diffraction studies of the ternary alloys (V,Mn)₂Ga₅. By W. J. KITCHINGMAN and P. L. NORMAN,* *Metalurgy Department, University of Manchester Institute of Science and Technology, Sackville Street, Manchester M60 1QD, England*

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X-ray diffraction studies have been carried out on eleven alloys of the structure (V, Mn)₂Ga₅ across the ternary phase field between V₂Ga₅ and Mn₂Ga₅. The alloys form a complete series of solid solutions having a structure of the Mn₂Hg₅ type. The *a* lattice constant of the tetragonal unit cell varies smoothly from 8·9050 Å for Mn₂Ga₅ to 8·9892 Å for V₂Ga₅ whilst the *c* lattice constant shows little variation and has a value in the range 2·6981 to 2·7003 Å. The results support the view that the structure is primarily governed by the size of the gallium atoms.

The intermediate phases Mn₂Hg₅, V₂Ga₅ and Mn₂Ga₅ have a space group *P4/mbm* with 14 atoms per unit cell. The structure of Mn₂Hg₅ was established by De Wet (1961) using single-crystal methods. A similar structure has been reported for the alloy V₂Ga₅ by van Vucht, Bruning, Donkersloot & Gomes de Mesquita (1964) and for the alloy Mn₂Ga₅ by Meissner & Schubert (1965). The structure of these alloys may be discussed in terms of the notation of Frank & Kasper (1958, 1959). It is of a layer type and has some similarities to the σ phase and the β -tungsten (Cr₃Si) structure, both of which are found as intermediate phases in alloy systems containing transition-group elements. In the Frank & Kasper notation the Mn₂Hg₅ type structure (Fig. 1.) has a primary layer which is a tessellation of pentagons, squares and triangles and a secondary layer which is an array of simple squares. De Wet suggested that the cell dimensions are governed by the size of the primary-layer atoms of mercury which are packed more closely together than the secondary-layer atoms of manganese. In order to investigate this suggestion, a ternary system of the same structure was sought in which

Ces 3 derniers contacts entraînent la formation de chaînes parallèles à l'axe unique, ces chaînes se lient par N(11)···H(17) en plans, ce qui justifie la texture en feuillets des cristaux.

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the size of secondary-layer atoms could be varied whilst keeping the primary-layer atoms constant. The system (V₂Mn)₂Ga₅ is a suitable system, the primary-layer atoms being gallium, whilst the secondary-layer atoms vary from vanadium to manganese.

Eleven alloys were prepared from vanadium, manganese and gallium of better than 99·99% purity, the major impurities being iron and silicon of 200 ppm. The alloys were melted in an arc furnace under an argon pressure of 200 torr, each alloy being remelted after inversion in the furnace. In all alloys the weight loss was less than 2%. The alloys were chemically analysed and the compositions are shown in Table 1. The following heat treatment of the alloys was critical in the preparation of good single phase alloys. The cast alloys were annealed under argon in alumina tubes. The manganese-rich alloys were annealed at 800°C for 48 hours and then furnace-cooled over 48 hours. The vanadium-rich alloys were annealed at 1050°C for 48 hours and then furnace-cooled over a maximum of 60 hours. The ingots were powdered in a percussion mortar and sieved through 400 B.S. mesh. Stress-relieving anneals were carried out under argon, for 48 hours at 350°C for the manganese-rich alloys and 30 hours at 800°C for the

* Present address: Henry Wiggin Ltd., Hereford, England.

vanadium-rich alloys. Powder diffraction photographs were obtained using copper $K\alpha$ radiation, $\lambda K\alpha_1 = 1.54051 \text{ \AA}$, $\lambda K\alpha_2 = 1.54433 \text{ \AA}$. Accurate parameter measurements were obtained using the method of Kitchingman & Hoff (1966). Single-crystal Laue and rotation photographs were also obtained using the alloy $(V_{0.5}Mn_{0.5})_2Ga_5$.

Table 1. Chemical compositions and accurate lattice parameter determinations using the program of Kitchingman & Hoff (1966)

Composition by chemical analysis	Lattice constants (\AA) at 20°C	
	<i>a</i>	<i>c</i>
$Mn_{1.85}Ga_5$	8.9050 (2)	2.6993 (1)
$(Mn_{0.91}V_{0.12})_2Ga_5$	8.9121 (5)	2.6993 (3)
$(Mn_{0.79}V_{0.21})_2Ga_5$	8.9150 (3)	2.6981 (2)
$(Mn_{0.76}V_{0.24})_2Ga_5$	8.9320 (7)	2.6979 (1)
$(Mn_{0.59}V_{0.41})_2Ga_5$	8.9483 (3)	2.7000 (2)
$(Mn_{0.51}V_{0.54})_2Ga_5$	8.9450 (2)	2.7003 (2)
$(Mn_{0.38}V_{0.62})_2Ga_5$	8.9510 (6)	2.6995 (3)
$(Mn_{0.27}V_{0.77})_2Ga_5$	8.9571 (4)	2.7003 (1)
$(Mn_{0.22}V_{0.85})_2Ga_5$	8.9732 (1)	2.6993 (2)
$(Mn_{0.11}V_{0.92})_2Ga_5$	8.9781 (4)	2.6989 (2)
$V_{1.96}Ga_5$	8.9892 (3)	2.6981 (1)

The X-ray powder photographs were all similar, indicating they were the same single phase of the Mn_2Hg_5 type. Fifty-five lines were observed in the powder pattern of Mn_2Ga_5 and attempts were made to index them using the reported parameters of $a = 8.800 \text{ \AA}$, $c = 2.690 \text{ \AA}$. This failed to index the pattern fully. A redetermination of the parameters was made which suggested parameters $a = 8.905 \text{ \AA}$, $c = 2.690 \text{ \AA}$. Using these values the program fully indexed all observed lines. The indexing and parameter calculations were then carried out using similar starting parameters for all the alloys. In each case the patterns were fully indexed. The results are shown in Table 1. Attempts were made to obtain good single crystals of the ternary alloys but this was only possible for the alloy $(V_{0.5}Mn_{0.5})_2Ga_5$, the other alloys being polycrystalline or imperfect after various heat treatments. The single crystal investigated was needle-like, its axis corresponding to the [001] axis. The tetragonal cell gave $c = 2.698 \pm 0.005 \text{ \AA}$ which is in good agreement with the powder data.

The alloys V_2Ga_5 and Mn_2Ga_5 form a complete series of solid solutions of the form $(V_1Mn)_2Ga_5$ with the structure of Mn_2Hg_5 . The *a* lattice constant varies from 8.9892 \AA for V_2Ga_5 to 8.9050 \AA for Mn_2Ga_5 . The *c* lattice constant shows little variation being 2.6981 \AA for V_2Ga_5 and 2.6993 \AA for Mn_2Ga_5 .

The atomic radius of gallium is 1.39 \AA . As the *c* lattice constant of the unit cell is close to 2.70 \AA , either there is some overlap of the *p* orbitals of the gallium atoms or the atoms are subject to some distortion. The fact that the *c* lattice constant shows so little variation with composition in the ternary alloys suggests a strong bond in the *c* axis direction between gallium atoms, and favours the overlap of the *p* orbitals. The variation of the *a* lattice constant with composition shows that the packing of the gallium atoms can vary a little in the *a*-axis direction in order to accommodate secondary layer atoms of varying size. The

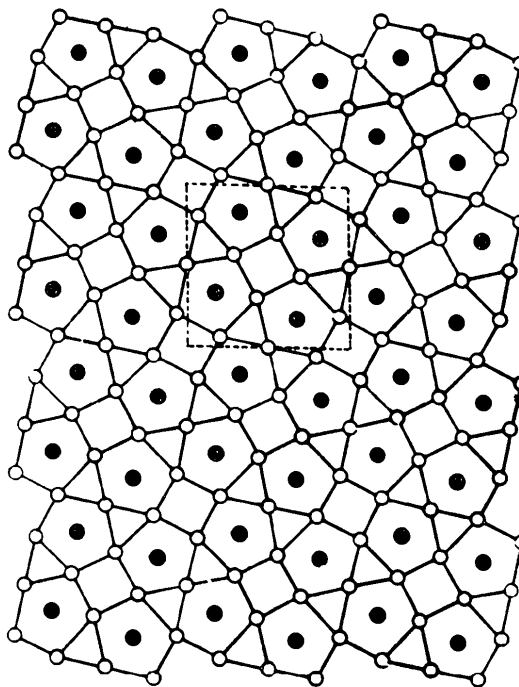


Fig. 1. The Mn_2Hg_5 structure showing the layer network in the direction of the *c* axis. The unit cell is shown by the dashed lines (De Wet, 1961). In the present work the open circles represent gallium atoms and the filled circles manganese or vanadium atoms.

decrease in the *a* lattice constant of 0.1 \AA on the addition of manganese to V_2Ga_5 agrees with the smaller value of the radius of the manganese atom (1.31 \AA) compared with a radius of the vanadium atom (1.36 \AA).

It is concluded that the dimensions of the structure are governed by the strong bond between the primary layers of atoms in the *c*-axis direction of the crystal structure. The packing within each primary layer is looser and may be varied in order to accommodate the size of the secondary layer atoms.

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