# The Crystal Structure of Mo<sub>6</sub>Ga<sub>31</sub>, a Hypersymmetrical Structure Solved by Direct Methods

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Mo<sub>6</sub>Ga<sub>31</sub> is monoclinic and crystallizes in a new structure type: a=9.517 (3), b=16.067 (4), c=16.995 (5) Å,  $\beta=95.09$  (2)°, space group  $P2_1/c$ , Z=4,  $D_x=7.0$  g cm<sup>-3</sup> (single-crystal diffractometry, refinement by the least-squares method,  $R_{|F|>4\sigma}=6\%$ ). The most important structural features are MoGa<sub>10</sub> polyhedra arranged at the corners of distorted cubes and gallium layers penetrating the crystal structure in different directions. There are no Mo-Mo contacts, no Ga-Ga pairs but some very short Mo-Ga distances. Not all sites have full occupancy, suggesting that the 'MoGa<sub>5</sub>-phase' has a range of homogeneity between the limits Mo<sub>6</sub>Ga<sub>31</sub> and Mo<sub>7</sub>Ga<sub>30</sub>. This crystal structure is compared with other complex structures of transition metal gallides and aluminides. In order to solve the crystal structure by use of direct methods renormalization of the structure factors was necessary.

#### Introduction

It is surprising still to find binary systems of metallic compounds on which practically no X-ray examinations have been carried out. Such is the case for the molybdenum-gallium system, whose phase diagram was only recently published (Bornand, Siemens & Oden, 1973). It gives the approximate stoichiometry and decomposition temperature for two intermetallic compounds: Mo<sub>3</sub>Ga and MoGa<sub>5</sub>. Mo<sub>3</sub>Ga crystallizes with the  $\beta$ -W type structure (A15), which is a structure of considerable interest for low-temperature physicists. Compounds with this structure have superconducting transition temperatures that depend strongly on the valence electron concentration (v.e.c.) and range from <1 up to 22°K, the highest value measured so far.

The search for superconductors with high transition temperatures revealed the existence of a Ga-rich phase, which was first denoted 'MoGa<sub>4</sub>' (Matthias, Compton & Corenzwit, 1961) but corresponds to the MoGa<sub>5</sub> phase mentioned above. X-ray powder analysis suggested that this compound has a rather complex crystal structure. It was therefore surprising to find relatively high superconducting transition temperatures between 8 and 9°K. Of even greater interest however was the magnetic behaviour at low temperatures. MoGa<sub>5</sub> is diamagnetic, having a critical field  $H_{c2}$  of 74 kG (Fischer, 1972). Moreover, by dissolving very small amounts of 'magnetic impurities' like Mn in the crystal structure, anomalous values of the magnetic moment ('giant moments') of 7.5 B.M. per atom were observed and experimental evidence for the 'internal compensation effect' predicted by Jaccarino & Peter was obtained (Jaccarino & Peter, 1962; Fischer, Jones, Bongi, Frei & Treyvaud, 1971). In order to continue with theoretical calculations on these findings, the knowledge of the exact composition and the environment of the transition element in this compound is of importance. It became, therefore highly desirable to

solve its crystal structure. The reasons for such an investigation not having been carried out up to this time are the difficulties of obtaining single crystals suitable for X-ray examination and the very particular crystal structure of  $MoGa_5$  which has resisted standard methods of X-ray structure analysis. The failure to obtain good single crystals was partly due to the absence of an accurate phase diagram indicating the temperature and composition range of the  $MoGa_5$  phase.

It was therefore decided to perform a preliminary X-ray study on the entire Mo-Ga system in order to gain insight into the phase relations.

#### Sample preparation

High purity gallium was added to molybdenum powder  $(<10\mu m)$  in compositions covering the entire range of the phase diagram. The samples were heated in alumina crucibles up to 1100°C under 1 atm of pure argon and held at this temperature until all the molybdenum powder was dissolved in the melt. Then the temperature was slowly lowered until the melt solidified. During this procedure, curious phenomena were observed with samples in the composition range between MoGa<sub>4</sub> and MoGa<sub>6</sub>. At temperatures of about 700°C, the melt suddenly increased substantially in volume, decomposing into a very fine and loosely-packed powder at lower temperatures. A similar observation seems to have been made in the Pt-Al system (Edshammar, 1966). In order to interpret this phenomenon, it is attractive to speculate on the formation of Mo-Ga clusters in the melt at temperatures close to solidification (see last paragraph).

#### X-ray powder analysis

The two prominent phases Mo<sub>3</sub>Ga and MoGa<sub>5</sub> form very quickly and are readily recognizable on powder photographs. Mo<sub>3</sub>Ga ( $\beta$ -tungsten type, A15, a = 4.94 Å) gives few and very sharp lines, whereas MoGa<sub>5</sub> has a very complex powder pattern characterized by many diffuse reflexion bands (Table 1). Guinier photographs suggested that this phase might have a homogeneity range between MoGa<sub>4.5</sub> and MoGa<sub>5.5</sub>. There was practically no change in the powder pattern over this range of composition, indicating that substitution of Mo and Ga atoms in the crystal structure was probable ( $r_{Ga} = 1.41$ ,  $r_{Mo} = 1.40$  Å).\*

## Table 1. Powder pattern of the MoGa<sub>5</sub> phase, Cu K $\alpha$ , $I_{calc}$ contains the Lp factor for a Guinier camera using a quartz monochromator

Only observed reflexions are included in the list.

| h | k l           | $d(\text{\AA})$                | $I_{obs}$                               | Icale |
|---|---------------|--------------------------------|---|-------|
| 0 | 2 3           | 4.62                           | vw                                      | 100   |
| 2 | 2 - 1         | 4.04 )                         |   | 461   |
| 1 | 2 3           | 4·04 Ì                         | US                                      | 461   |
| 0 | 4 0           | 4.02                           | S                                       | 220   |
| 1 | 0 - 4         | 4.00                           | \$                                      | 207   |
| 3 | 0 2           | 2.88                           | S                                       | 326   |
| 1 | 4 - 4         | 2.83                           | m, diff                                 | 452   |
| 3 | 1 3           | 2.62                           | 1.00                                    | 118   |
| 2 | 5 1           | 2.61                           | w, aiff                                 | 108   |
| 2 | 4 - 4         | 2.55                           | m, diff                                 | 320   |
| 3 | 4 2           | 2.34                           | ,                                       | 263   |
| 2 | 0 6           | 2.34                           | S                                       | 188   |
| 0 | 5 5           | 2.33                           |   | 127   |
| 2 | 6 - 1         | 2.32                           |   | 259   |
| 1 | 6 3           | 2.32                           |   | 192   |
| 3 | 2 - 5         | 2.32                           | S                                       | 226   |
| 0 | 2 7           | 2.32                           |   | 167   |
| ĩ | 5 - 5         | 2.30                           |   | 599   |
| ĩ | 2 - 7         | $\frac{1}{2}$ , $\frac{1}{30}$ | т                                       | 251   |
| 4 | $\bar{2} - 1$ | 2.28                           | т                                       | 241   |
| 1 | 5 5           | 2.23 )                         |   | 178   |
| 4 | 0 2           | 2.23                           | т                                       | 364   |
| 0 | 7 2           | $2.215^{\prime}$               |   | 298   |
| 3 | 5 1           | 2.215                          |   | 131   |
| 2 | 1 - 7         | 2.215                          | s, diff                                 | 102   |
| 3 | 3 4           | 2.213                          | , ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,, | 171   |
| 3 | 4 - 4         | 2.210                          |   | 219   |
| 1 | 4 6           | 2.206                          |   | 535   |
| 4 | 3 - 1         | 2·172                          |   | 187   |
| 1 | 7 - 2         | 2·168 }                        | m, diff                                 | 205   |
| 4 | 3 0           | <b>2</b> ·167                  |   | 227   |
| 2 | 2 - 7         | 2.154                          | w                                       | 299   |
| 3 | 5 - 3         | 2·140                          | m diff                                  | 245   |
| 3 | 25            | 2.135 ∫                        | m, agg                                  | 249   |
| 2 | 6 3           | 2.122                          | vw                                      | 117   |
| 4 | 1 3           | 2.101                          | nw                                      | 89    |
| 1 | 5 - 6         | 2.099 ∫                        | 0.11                                    | 91    |
| 4 | 4 - 2         | 2.020                          | 1).5                                    | 962   |
| 2 | 4 6           | <b>2</b> ·019 ∫                | 00                                      | 1000  |
| 0 | 8 0           | 2.008                          | S                                       | 514   |
| 2 | 0 - 8         | 2.000                          | \$                                      | 397   |
| 4 | 2 - 5         | 1.966                          | nw                                      | 60    |
| 1 | 80            | 1.965 (                        |   | 66    |

A list of the *d* values for most of the strong reflexions as well as their observed and calculated intensities is given in Table 1. Owing to overlap, accurate lattice parameters could not be derived from powder photographs. The following values were obtained from several single crystals measured on the automatic diffractometer: a=9.517 (3), b=16.067 (4), c=16.995 (5) Å,  $\beta=95.09$  (2)°. The experimental density was measured by displacement:  $\rho = 7.0$  (1) g cm<sup>-3</sup>.

## Preparation of single crystals

Samples in the composition range between  $MoGa_4$  and  $MoGa_6$  usually do not contain single crystals large enough for X-ray analysis. This is a consequence of the previously described anomaly of the melt yielding a powder of an estimated average grain size of a few microns. Annealing did not result in a substantial increase of this grain size, so that we tried to obtain single crystals in more gallium-rich samples.

One such sample contained well developed needles suitable for single-crystal analysis. It is difficult to state exact experimental conditions for growing these crystals, since they probably form only in a very restricted range of concentration (~MoGa<sub>s</sub>) and of temperature (~700 °C). These single crystals have 2/m symmetry, the needle axis corresponding to **a**. Precession photographs indicated the space group  $P2_1/c$ , the systematic extinctions being for h0l: l=2n+1 and for 0k0: k=2n+1.

## **Data collection**

Complete data sets of four different crystals were collected with an automatic single-crystal diffractometer (Philips PW1100) using  $\omega - 2\theta$  scans and Mo Ka radiation (graphite monochromator). The largest crystal ( $400 \times 50 \times 50 \ \mu$ m) was used for collecting very quickly most intensities in the Mo sphere (about 13000 independent reflexions). Such a relatively large number of data were measured in order to find a sufficiently great number of strong reflexions necessary for successful application of statistical methods. Owing to the very



Fig. 1. Theoretical N(z) curves and experimental distribution of normalized structure factors for MoGa<sub>5</sub>.

<sup>\*</sup> Metallic radii for coordination 12 compiled by Teatum, Gschneidner and Waber (Pearson, 1972).

special distribution of X-ray intensities of  $MoGa_5$ , an abnormally large fraction of reflexions had intensities too low for use by these methods.

Data sets for the other crystals of smaller size  $(25 \times 25 \times 200 \ \mu\text{m})$  were collected with higher precision and kept for later refinement of structure parameters. |F| values and their standard deviations were calculated as usual and small intensities were treated as follows:

if 
$$|F|^2 < \sigma_{1F|^2}$$
,  $|F|^2$  was replaced by  $\frac{1}{2}(|F|^2 + \sigma_{1F|^2})$ 

Correction for absorption ( $\mu_{MoGa5} = 370 \text{ cm}^{-1}$ ) was made applying the analytical method (de Meulenaer & Tompa, 1965) and using a computer program written by Tompa & Alcock (1969). The transmission factors varied between 0.27 and 0.18.

## The $|F|^2$ synthesis for MoGa<sub>5</sub>

A three-dimensional  $|F|^2$  synthesis was calculated for 250 000 grid points using 4500 independent reflexions.

It was surprising to find that despite the large number of about 150 atoms per unit cell, this map nevertheless revealed interesting features useful for the structure determination. Besides two prominent Harker peaks at (0, 0.26, 0.5) and (0.87, 0.5, 0.30) about 60 peaks had heights that were greater than 10% of the origin peak. This can only be explained by the presence of a large number of equal interatomic vectors in the crystal structure. About half of all strong peaks were located on, or very close to, positions that could be attributed to a cubic cell with a = 5.76 Å. This cell was especially well visible in the four zones {102}, {301},  $\{872\}, \{8\overline{7}2\}$  corresponding to the directions of the body diagonals in this cube. Approximate threefold symmetry is visible in these sections, but not so in upper layers. This cubic cell can therefore be only a very crude approximation to the substructure of MoGa<sub>5</sub>. Furthermore, many high peaks in the  $|F|^2$  map still remained uninterpreted and it finally turned out to be impossible to proceed any further by use of Patterson methods alone. Current methods like superposition

Table 2. Atomic fractional coordinates  $(\times 10^4)$ , occupancy factors and their least-squares values  $d(\times 10^2)$ , an thermal parameters  $(\times 10^2)$  with their standard deviations in brackets, for Mo<sub>6</sub>Ga<sub>31</sub>, space group P2<sub>1</sub>/c (No. 14)

All atoms are in equipoint 4(e) except for Ga(31) in 2(a) and Ga(32) in 2(c).

|         | x        | у         | z                 | Occ | upancy  | $B(Å^2)$ |
|---------|----------|-----------|-------------------|-----|---------|----------|
| Ga(1)   | 180 (8)  | 2456 (5)  | 122 (5)           | 1.0 | 102 (4) | 85 (15)  |
| Ga(2)   | 7234 (8) | 2008 (5)  | 194 (4)           | 1.0 | 102 (3) | 111 (14) |
| Ga(3)   | 6992 (9) | 28 (6)    | 418 (5)           | 0.9 | 90 (3)  | 158 (15) |
| Ga(4)   | 6273 (6) | 3844 (6)  | 471 (3)           | 1.0 | 101 (3) | 75 (12)  |
| Ga(5)   | 4592 (9) | 850 (5)   | 735 (5)           | 0.9 | 91 (3)  | 141 (15) |
| Ga(6)   | 2812 (9) | 2562 (6)  | 913 (5)           | 1.0 | 100 (3) | 102 (16) |
| Ga(7)   | 9106 (7) | 3791 (6)  | 1073 (4)          | 1.0 | 99 (3)  | 100 (13) |
| Ga(8)   | 9508 (8) | 1218 (6)  | 1077 (5)          | 1.0 | 99 (3)  | 90 (13)  |
| Ga(9)   | 5643 (9) | 2488 (6)  | 1381 (5)          | 1.0 | 99 (3)  | 78 (14)  |
| Ga(10)  | 1669 (7) | 3845 (6)  | 1836 (4)          | 1.0 | 99 (3)  | 73 (12)  |
| Ga(11)  | 2223 (8) | 1351 (5)  | 1927 (4)          | 1.0 | 100 (3) | 94 (16)  |
| Ga(12)  | 8439 (9) | 2416 (5)  | 2041 (5)          | 1.0 | 102 (4) | 64 (16)  |
| Ga(13)  | 8907 (9) | 33 (5)    | 2091 (5)          | 1.0 | 101 (4) | 75 (15)  |
| Ga(14)  | 6580 (6) | 3841 (6)  | 2400 (4)          | 1.0 | 103 (2) | 97 (11)  |
| Ga(15)  | 5026 (9) | 1309 (6)  | 2486 (5)          | 1.0 | 98 (3)  | 89 (13)  |
| Ga(16)  | 4014 (9) | 2955 (5)  | 2748 (5)          | 1.0 | 100 (3) | 121 (15) |
| Ga(17)  | 4044 (8) | 4702 (5)  | 2813 (5)          | 1.0 | 101 (3) | 106 (14) |
| Ga(18)  | 1066 (9) | 2566 (6)  | 2875 (5)          | 1.0 | 98 (4)  | 79 (15)  |
| Ga(19)  | 1563 (9) | 204 (5)   | 3035 (5)          | 1.0 | 100 (3) | 96 (15)  |
| Ga(20)  | 7954 (8) | 1210 (6)  | 3086 (4)          | 1.0 | 100 (3) | 81 (14)  |
| Ga(21)  | 4396 (8) | 203 (5)   | 3641 (5)          | 1.0 | 99 (3)  | 80 (14)  |
| Ga(22)  | 8222 (8) | 2859 (5)  | 3663 (5)          | 1.0 | 98 (3)  | 98 (15)  |
| Ga(23)  | 7986 (8) | 4729 (5)  | 3681 (4)          | 1.0 | 101 (3) | 102 (14) |
| Ga(24)  | 707 (9)  | 3804 (6)  | 3983 (5)          | 1.0 | 100 (2) | 90 (11)  |
| Ga(25)  | 5686 (9) | 1959 (4)  | 4019 (5)          | 1.0 | 102 (3) | 95 (11)  |
| Ga(26)* | 5641 (9) | 3846 (6)  | 4022 (5)          | 1.0 | 98 (2)  | 121 (10) |
| Ga(27)  | 740 (8)  | 1328 (5)  | 4049 (5)          | 1.0 | 97 (3)  | 91 (14)  |
| Ga(28)  | 7317 (9) | 51 (5)    | 4200 (5)          | 1.0 | 97 (3)  | 75 (15)  |
| Ga(29)  | 3271 (7) | 2971 (5)  | 4341 (4)          | 1.0 | 104 (3) | 103 (13) |
| Ga(30)  | 3459 (7) | 1224 (6)  | 4890 ( <b>6</b> ) | 1.0 | 99 (3)  | 72 (12)  |
| Ga(31)  | 0 `´     | 0 `´      | 0                 | 1.0 | 96 (4)  | 62 (23)  |
| Ga(32)  | 0        | 5000      | 0                 | 0.9 | 90 (4)  | 166 (27) |
| Mo(1)   | 1848 (6) | 1131 (4)  | 403 (3)           | 1.0 | 100     | 39 (9)   |
| Mo(2)   | 4247 (5) | 3839 (4)  | 1409 (3)          | 1.0 | 98 (2)  | 24 (7)   |
| Mo(3)   | 7000 (6) | 1109 (4)  | 1566 (3)          | 1.0 | 98 (2)  | 10 (10)  |
| Mo(4)   | 9378 (5) | 3819 (4)  | 2619 (3)          | 1.0 | 97 (2)  | 20 (8)   |
| Mo(5)   | 3092 (6) | 1585 (́4) | 3395 (3)          | 1.0 | 97 (2)  | 43 (10)  |
| Mo(6)   | 8299 (6) | 1489 (4)  | 4606 (3)          | 1.0 | 97 (2)  | 44 (11)  |

\* The site Ga(26) in  $Mo_7Ga_{30}$  is probably occupied by molybdenum.

minimum functions, image seeking or vector verification all suffer from the annoying presence of multiply superposed peaks and often fail to solve hypersymmetrical crystal structures at all. Therefore, an attempt was made to use statistical methods.

#### Calculation of normalized structure factors

Owing to the presence of building blocks in the structure of MoGa<sub>5</sub>, many regions of  $\sin \theta/\lambda$  had abnormally high intensity averages. This had been recognized on powder patterns where many of the strongest intensities are grouped around *d* values of 2 and 4 Å. It was therefore difficult to derive scale and temperature factors from a Wilson plot. An overall temperature factor of B=1.0 Å<sup>2</sup> was finally used for calculation of the normalized structure factors and the scale factor was fixed by imposing the condition  $\langle E_{hkl}^2 \rangle =$ 1.0. An N(Z) plot (Fig. 1) revealed that the distribution of structure factors for MoGa<sub>5</sub> is 'hypersymmetric' (Rogers & Wilson, 1953).

#### Renormalization

Several attempts to use this original set of |E| values for statistical methods failed to yield the correct structure. This was due to the presence of the previously mentioned building blocks. Such sub-units usually give rise to a non-Gaussian distribution of structure factors and violate the assumption of randomness under which probability formulae of sign determination are derived. From inspection of the  $|F|^2$  synthesis it was concluded that the most likely structure of these sub-units might correspond to the atom arrangement in the NiHg<sub>4</sub> type [space group *Im3m*, 2Mo in (*a*), 8 Ga in (*c*): Bauer, Nowotny & Stempfl (1953)].

In order to account for these sub-units, renormalization of the |E| values was necessary (Hauptman & Karle, 1959; Hauptman, 1964). This was done by subtracting the contribution of the subcell from the observed intensities and by recalculating normalized structurefactors with this new set of corrected intensities. The final set of renormalized structure factors used in the symbolic addition method contained 336 |E| values greater than 1.5.

#### Symbolic addition

After generating about 4000 triple-product sign relationships by use of the computer program LSAM(Main, Woolfson, Germain, 1972) three reflexions were chosen in order to define the origin in the unit cell according to the known selection rules. Owing to the presence of building blocks in the structure, care had to be taken not to select more than one reflexion out of the subset of structure factors corresponding to the cubic cell used for renormalizing the |E| values. The following reflexions were used:

$$1,2,13, 3,13,\overline{3}, 146$$
 (origin)  
 $5,4,\overline{12}, 5,17,3, 10,6,\overline{1}, 4,17,\overline{17}$  (symbols  $a,b,c,d$ ).

The symbolic addition procedure resulted in multiple solutions of which the ones with the highest figures of merit were used for calculating |E| maps. One of them (the fourth best) contained essentially the correct structure. This was not immediately realized, however, for the following reasons. Firstly, the exact number of atoms expected in the asymmetric unit was not known, since the specific gravity of MoGa<sub>5</sub> could only be measured with low accuracy. Secondly, the amplitude termination effects (Burgi & Dunitz, 1971) in |E| maps of hypersymmetrical crystal structures result inevitably in 'ghost-peaks' making it often difficult to sort out correct atom positions. The third and most discouraging difficulty was the fact that the conventional R values calculated for all the different solutions obtained from the statistical methods were practically identical and always very close to the theoretical values of a 'completely wrong' structure. Even during the initial refinement of the correct structure model by  $F_o$  syntheses, this R value did not drop significantly, so that considerable computational effort was necessary to recognize which set of |E| values gave a refinable electrondensity map and which did not. This was finally achieved with set 4 at an R value of 55%. Successive refinement by electron-density methods resulted in the recognition of 38 atomic sites per asymmetric unit. Throughout this procedure weighted Fourier coefficients were used (Woolfson, 1970).

#### Refinement of the structure

Refinement of the structure by  $F_o$  and  $\Delta F$  syntheses was slow and did not reduce the convential R value below 20%. Least-squares methods gave better convergence by comparison, but suffered from the presence of strong parameter correlations and from partially occupied sites. Therefore, occupancy factors and positional as well as thermal parameters had to be refined in separate stages. The full-matrix least-squares program *ORXFLS3* (Busing *et al.*, 1971b) was used and correction for extinction and anomalous dispersion was made (g' = 0.0003; Ga:  $\Delta f' = 0.2$ ,  $\Delta f'' = 1.7$ ; Mo:  $\Delta f' = -1.7$ ,  $\Delta f'' = 0.9$ ).

Atomic scattering factors were taken from International Tables for X-ray Crystallography (1962). The weighting scheme  $w = 1/\sigma^2$  was applied and refinement was considered complete when the last shifts of the parameters were 0.1 of their estimated standard deviations (e.s.d.). The final 184 parameters and their e.s.d.'s are listed in Table 2. The residual  $R = \sum \Delta F_o / \sum |F_o|$  is 6% for 1500 reflexions with  $|F| > 4\sigma$  and 10% for 3200 reflexions with  $|F| > \sigma$ . A list of observed and calculated structure factors is given in Table 4. A final difference electron-density map revealed no abnormal features and confirmed the partial occupancies of the four atom sites.

#### Composition of MoGa<sub>5</sub>

Refinement of the occupancy factors for the 38 different atomic sites revealed that at least 6 of them are occupied by molybdenum atoms and that many sites have more or less pronounced defect character. Especially one site  $(x, y, z \equiv 0.564, 0.385, 0.402)$ , originally identified as an Mo atom, had an occupancy that corresponded to a gallium atom rather than to a partially occupied Mo. This assumption is supported by the interatomic distances from this atom to those coordinating it. They are significantly larger than the Mo-Ga distances observed in other coordination shells and correspond rather to Ga-Ga distances (Table 3).

#### Table 3. Interatomic distances and coordination number

(a) Interatomic distances (Å), with e.s.d.'s, for  $Mo_6Ga_{31}$ . In cluded are all Mo-Ga distances less than 4 Å.

| Mo(1)-G      | fa(24)                  | 2.559 (12)             | Mo(4)-          | Ga(24)      | 2.541 (11)             |
|--------------|-------------------------|------------------------|-----------------|-------------|------------------------|
| G            | Ga(31)                  | 2.579 (7)              |                 | Ga(13)      | 2.563 (11)             |
| G            | Ga(6)                   | 2.596 (13)             |                 | Ga(12)      | 2.587 (11)             |
| G            | Ga(8)                   | 2.596 (11)             |                 | Ga(18)      | 2.588 (12)             |
| G            | Ga(11)                  | 2·607 (11)             |                 | Ga(19)      | 2.609(11)              |
| G            | la(3)                   | 2.629 (13)             |                 | Ga(7)       | 2.617(10)              |
| Ğ            | fa(5)                   | 2.661(12)              |                 | Ga(10)      | 2.654 (9)              |
| Ğ            | fa(1)                   | 2.672(12)              |                 | Ga(14)      | 2.656 (8)              |
| G            | $a_{2}(23)$             | 2.735(11)              |                 | $G_{2}(22)$ | 2.661(11)              |
| G            | a(23)                   | 2.758(11)              |                 | $G_{a}(23)$ | 2.752(10)              |
| N            | Aean valu               | e: 2.639               |                 | Mean val    | ue: $2.623$            |
| Ma(2) C      |                         | 2.547(11)              | $M_{\alpha}(5)$ | Go(15)      | 2.544(11)              |
| MO(2) - G    | $\operatorname{Fa}(21)$ | 2.347(11)              | WI0(5)-         | Ga(13)      | 2.544(11)              |
| 0            | 5a(9)                   | 2.348(12)              |                 | Ga(21)      | 2.501(11)<br>2.584(10) |
| 6            | Ja(6)                   | 2.200(12)              |                 | Ga(11)      | 2.364(10)              |
| G            | ja(4)                   | 2.607 (9)              |                 | Ga(18)      | 2.282 (12)             |
| G            | ja(28)                  | 2.609 (11)             |                 | Ga(30)      | 2.600 (10)             |
| G            | fa(10)                  | 2.620 (9)              |                 | Ga(27)      | 2.619 (11)             |
| G            | Ga(30)                  | 2.626 (9)              |                 | Ga(16)      | 2.644 (12)             |
| G            | Ga(14)                  | 2·665 (9)              |                 | Ga(25)      | 2.667 (12)             |
| G            | Ga(16)                  | 2.709 (11)             |                 | Ga(19)      | 2.694 (12)             |
| G            | Ga(17)                  | 2.781 (11)             |                 | Ga(29)      | 2.744 (11)             |
| Ν            | lean valu               | e: 2.628               |                 | Mean val    | ue: 2·624              |
| $M_0(3) - G$ | fa(15)                  | 2.568 (11)             | Mo(6)-          | Ga(1)       | 2.562(11)              |
|              | fa(9)                   | 2.569(12)              |                 | Ga(28)      | 2.565(11)              |
| ē            | fa(12)                  | 2.595(11)              |                 | Ga(7)       | 2.583 (11)             |
| Ğ            | fa(8)                   | 2.603(11)              |                 | Ga(4)       | 2.583 (9)              |
| Ğ            | $f_{a(13)}$             | 2.607(11)              |                 | Ga(27)      | 2.598 (11)             |
| G            | $F_{a}(3)$              | 2.607(11)<br>2.612(12) |                 | $G_{a}(20)$ | 2.614(11)              |
|              | a(5)                    | 2.617(12)              |                 | $G_{2}(25)$ | 2.704(12)              |
|              | a(3)                    | 2.017(12)              |                 | $G_{2}(22)$ | 2.720(11)              |
|              | $S_{a}(20)$             | 2.000(10)              |                 | Ga(22)      | 2.824(11)              |
| 0            | ra(17)                  | 2.720(11)              |                 | Ga(2)       | 2.034(11)              |
| G            | Ja(2)                   | 2.769 (11)             |                 | Ga(32)      | 2.933 (7)              |
| N            | lean valu               | e: 2.633               |                 | Mean val    | ue: 2·670              |
| Ga(26)*-     | -Ga(23)                 | <b>2</b> ·751 (13)     |                 |             |                        |
|              | Ga(29)                  | 2.752 (13)             |                 |             |                        |
|              | Ga(2)                   | 2·759 (14)             |                 |             |                        |
|              | Ga(17)                  | <b>2·806</b> (14)      |                 |             |                        |
|              | Ga(16)                  | 2.923 (15)             |                 |             |                        |
|              | Ga(14)                  | 2.972 (12)             |                 |             |                        |
|              | Ga(22)                  | 3·031 (13)             |                 |             |                        |
|              | Ga(25)                  | 3.032 (13)             |                 |             |                        |
|              | Ga(3)                   | 3.166 (15)             |                 |             |                        |
|              | Ga(5)                   | 3.197(15)              |                 |             |                        |
|              | Ga(5)                   | 3.257 (15)             |                 |             |                        |
|              | $G_{a}(3)$              | 3.348(14)              |                 |             |                        |
|              | $\operatorname{Sa}(J)$  | 5 540 (14)             |                 |             |                        |

Mean value: 3.000

\* The site Ga(26) may also be occupied by molybdenum.

#### Table 3 (cont.)

(b) Coordination number (CN) for the Ga atoms in  $Mo_6Ga_{31}$ and number of Mo and Ga atoms ( $n_{Mo}$ ,  $n_{Ga}$ ) within a sphere of 3.5 Å around each Ga atom. The shortest Ga–Ga contact,  $d_{min}$ (Ga–Ga) (Å), is given for each polyhedron.

|        | CN | n <sub>Mo</sub> | n <sub>Ga</sub> | d <sub>min</sub> (Ga-Ga) |
|--------|----|-----------------|-----------------|--------------------------|
| Ga(1)  | 10 | 2               | 8               | 2.680                    |
| Ga(2)  | 12 | 2               | 10              | 2.739                    |
| Ga(3)  | 14 | 2               | 12              | 2.732                    |
| Ga(4)  | 10 | 2               | 8               | 2.759                    |
| Ga(5)  | 14 | 2               | 12              | 2.732                    |
| Ga(6)  | 10 | 2               | 8               | 2.693                    |
| Ga(7)  | 9  | 2               | 7               | 2.660                    |
| Ga(8)  | 10 | 2               | 8               | 2.664                    |
| Ga(9)  | 10 | 2               | 8               | 2.739                    |
| Ga(10) | 9  | 2               | 7               | 2.660                    |
| Ga(11) | 10 | 2               | 8               | 2.693                    |
| Ga(12) | 10 | 2               | 8               | <b>2</b> ·696            |
| Ga(13) | 10 | 2               | 8               | 2.664                    |
| Ga(14) | 13 | 2               | 11              | 2.837                    |
| Ga(15) | 10 | 2               | 8               | 2.752                    |
| Ga(16) | 13 | 2               | 11              | 2.810                    |
| Ga(17) | 12 | 2               | 10              | <b>2</b> ·789            |
| Ga(18) | 10 | 2               | 8               | <b>2·</b> 77 <b>3</b>    |
| Ga(19) | 9  | 2               | 7               | 2.661                    |
| Ga(20) | 10 | 2               | 8               | <b>2</b> ·696            |
| Ga(21) | 10 | 2               | 8               | 2.753                    |
| Ga(22) | 13 | 2               | 11              | 2.821                    |
| Ga(23) | 13 | 2               | 11              | 2.751                    |
| Ga(24) | 10 | 2               | 8               | 2.710                    |
| Ga(25) | 13 | 2               | 11              | <b>2</b> ·797            |
| Ga(26) | 12 | -               | 12              | 2.751                    |
| Ga(27) | 9  | 2               | 7               | 2.661                    |
| Ga(28) | 9  | 2               | 7               | 2.707                    |
| Ga(29) | 12 | 2               | 10              | 2.752                    |
| Ga(30) | 9  | 2               | 7               | <b>2·70</b> 7            |
| Ga(31) | 10 | 2               | 8               | 2.710                    |
| Ga(32) | 8  | 2               | 6               | 2.785                    |

Analysis of the single crystal by a microprobe\* indicated a composition of  $MoGa_{5\cdot1\pm0\cdot1}$ , which is in good agreement with the formula  $Mo_6Ga_{31}$ . It is however likely that  $MoGa_5$  has a domain of homogeneity between  $Mo_6Ga_{31}$  and  $Mo_7Ga_{30}$ , and that the change in composition over this range is conditioned by gradually replacing one molybdenum atom by one gallium atom.

In order to find evidence for this assumption, data sets of different crystals were refined, in the hope that the occupancy factor of the site with occupational disorder [Ga(26)] might change. The result, however, was negative. This is certainly related to the fact that large needles form peritectically only in a small concentration and temperature range at the Ga-rich limit of the phase, and therefore always have the composition  $Mo_6Ga_{31}$ .

There is, however, one additional detail worth mentioning: comparison of the powder diffraction patterns of samples  $Mo_6Ga_{31}$  and  $Mo_7Ga_{30}$  with the calculated intensities (Yvon, Jeitschko & Parthé, 1969) revealed some small discrepancies. This indicates that

<sup>\*</sup> These analyses were carried out by M Burri, Institut de Physique Expérimentale, Université de Lausanne and M Bertrand, Département de Minéralogie, Université de Genève.

# Table 4. Observed and calculated structure factors for Mo<sub>6</sub>Ga<sub>31</sub>

The columns contain from left to the right: k, l,  $F_{obs}$ ,  $F_{calc}$ . Only reflexions with  $|F| > 4\sigma$  are included.

| Okl  | 13-15 399 387<br>13-16 155 162   | 18-11 138 116<br>10 -7 406 416   | 6-13 146 164<br>7-12 175 164<br>7-11 402 512  | 5 9 168 191<br>5 7 671 626  | 2 -5 406 477<br>2 -7 153 176  | 1 9 248 227   | 6ki  | 1-16 168 150<br>2-10 168 169  | 6 10 172 153<br>6 7 295 244   |
|--|--|--|---|---|---|---|--|---|---|
| 8 -6 180 169<br>8 -6 218 229<br>8-10 250 208<br>1-12 167 177<br>1-11 264 263<br>1 -9 201 192<br>- 4 70 710     | 13 -5 218 211<br>13 -6 261 269<br>13 -1 164 105<br>13 - 239 269<br>13 5 250 211<br>13 13 172 163<br>13 17 27           | 10 +2 124 152<br>10 -1 187 157<br>10 0 206 209<br>10 2 152 177<br>10 3 334 334<br>10 4 160 186   | 7 -8 181 149<br>7 -2 121 109<br>7 0 392 390<br>7 1 319 326<br>7 2 228 211<br>7 9 211 193                          | 5 5 240 236<br>5 3 328 321<br>5 1 636 615<br>5 0 286 281<br>5 -2 327 323<br>5 +3 856 672                          | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 1 +6 158 155<br>1 -9 131 160<br>1-16 171 168<br>2-15 512 517<br>2-11 123 96<br>2 -9 233 228<br>2 -9 142       | $\begin{array}{c} 3 10 & 515 & 517 \\ 3 & 6 & 6 & 657 \\ 0 & 6 & 260 & 256 \\ 3 & 4 & 1159 & 5109 \\ 0 & -2 & 403 & 427 \\ 1 & -6 & 766 & 745 \end{array}$ | 2 -8 181 201<br>2 -7 160 109<br>2 -3 319 321<br>2 3 431 421<br>2 4 139 122<br>2 7 201 173                 | 6 -1 143 103<br>6 -3 664 550<br>6 -7 396 415<br>6-13 158 158<br>7-15 196 233<br>7-14 243 250                    |
| 1 -7 238 238<br>1 -7 238 238<br>1 8 381 769<br>1 -9 178 142<br>1 11 265 263<br>1 12 150 137                    | 14 11 164 205<br>14 21 155 199<br>14 1 226 252<br>14 0 347 350<br>14 -1 246 252<br>14 -2 204 199                       | 10 6 343 337<br>10 6 249 208<br>10 9 367 335<br>10 13 221 203<br>11 12 182 184<br>11 8 469 430   | 5 12 194 109<br>6 6 214 225<br>8 2 25 2 239<br>8 -1 113 96<br>8 -4 126 108<br>8 -6 117 139<br>6 -7 143 96         | 5-4 336 396<br>5-12 188 196<br>5-14 150 151<br>6-15 272 284<br>6-12 162 140<br>6 -7 122 133<br>6 -5 215 284       | 3 1 149 156<br>3 14 143 190<br>4 15 177 188<br>4 14 212 198<br>4 8 290 244<br>4 223 208                           | 2 1 372 344<br>2 3 421 427<br>2 9 260 242<br>2 11 722 707<br>2 14 139 84<br>3 18 300 269                      | 0-8 264 272<br>0-14 267 303<br>1-14 182 172<br>1-11 140 153<br>1-8 535 516<br>1-7 378 363  | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 7 =9 187 189<br>7 +8 309 329<br>7 =6 203 212<br>7 =3 334 356<br>7 =2 482 482<br>7 8 207 210<br>7 2 288 262      |
| 2 15 236 279<br>2 7 568 555<br>2 3 236 22A<br>2 -3 216 228<br>2 -7 560 555<br>2 -11 17 91                      | 14 -4 152 148<br>14-11 197 205<br>15-12 183 155<br>15 -8 380 404<br>15 -2 541 518<br>15 2 534 518                      | 11 6 397 380<br>11 2 236 262<br>11 0 152 179<br>11 -1 156 155<br>11 -3 155 166<br>11-12 317 345  | 8 -8 1197 1188<br>8 -9 366 399<br>8-11 189 179<br>9-10 169 219<br>9 -9 658 652<br>9 -8 417 451                    | 6 -1 254 243<br>6 8 122 82<br>6 1 345 334<br>6 3 271 264<br>8 5 515 511<br>6 7 172 176                            | 4 8 156 148<br>4 -1 158 164<br>4 -2 1739 1821<br>4 -3 206 217<br>4 -4 124 114<br>4 -7 154 174                     | 3 9 351 350<br>3 7 165 152<br>3 6 169 116<br>3 5 126 130<br>3 -3 167 183<br>3 -6 351 187<br>7 -6 257 257      | 1 -5 271 264<br>1 -6 239 217<br>1 -2 182 210<br>1 -1 171 163<br>1 5 593 583<br>1 6 391 379<br>1 8 286 288  | 3 - 8 193 214<br>3 - 9 304 326<br>3 - 15 167 182<br>4 - 13 185 164<br>4 - 10 497 526<br>4 - 6 442 451     | 3 0 254 250<br>5 -1 293 299<br>5 -2 197 193<br>5 -6 442 448<br>3 -5 155 160<br>5 -8 160 185                     |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$   | 15 12 159 155<br>1kl   | 12-13 176 198<br>12 -7 228 234<br>17 -5 247 237<br>12 -4 922 908<br>17 -3 266 268<br>12 -2 133 128   | 9 -5 154 146<br>9 -3 233 222<br>9 1 119 133<br>9 3 170 164<br>9 6 174 164<br>9 7 375 370                          | 6 9 721 719<br>6 15 306 308<br>7 14 367 359<br>7 13 287 292<br>7 8 239 216<br>7 7 180 200                         | 4 -9 169 178<br>5-11 139 100<br>5 -9 263 298<br>5 -1 265 296<br>5 -7 206 213<br>5 -3 305 327                      | 3 -9 254 311<br>3-10 258 293<br>4-12 829 857<br>4-10 253 275<br>4-9 243 240<br>4-8 349 376                    | 1 9 392 369<br>2 6 149 149<br>7 5 399 391<br>2 3 129 114<br>2 1 420 426<br>2 -3 227 249  | 4 3 173 176<br>4 4 713 698<br>4 6 211 209<br>4 10 194 170<br>4 12 165 145<br>4 14 340 313                 | 3-10 275 298<br>3-14 384 435<br>3-15 243 240<br>3-11 219 205<br>3-3 171 148<br>3-1 445 440<br>3 9 193 202       |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$   | 0-10 447 454<br>0-4 528 554<br>0 2 79 92<br>0 6 460 446<br>0 18 855 864<br>0 12 357 360                                | 12 0 140 123<br>12 6 217 218<br>12 7 187 152<br>12 8 210 218<br>13 11 348 336<br>13 7 184 157<br>13 5 709 687  | 9 10 286 197<br>9 11 578 549<br>10 9 181 166<br>10 6 343 359<br>10 5 305 385<br>10 3 189 155<br>10 -1 219 248     | 7 6 141 194<br>7 5 162 155<br>7 3 211 194<br>7 8 318 297<br>7 -6 325 393<br>7 -7 202 214<br>F-10 160 160          | 5 -2 231 251<br>5 +1 529 521<br>5 0 127 135<br>5 2 125 110<br>5 7 350 313<br>5 9 155 153                          | 4 -7 160 161<br>4 -6 229 244<br>4 -5 118 128<br>4 -3 290 300<br>4 2 243 245<br>4 6 278 283<br>4 6 153 152     | 2 +5 192 187<br>2 -9 641 614<br>3 -12 164 184<br>3 -9 204 202<br>3 -4 232 257<br>3 -3 210 186<br>3 0 145 140   | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  |
| 3 14 199 194<br>• 1• 883 472<br>• 13 270 278<br>• 12 36• 365<br>• 11 1•6 162<br>• 19 369 793                   | 1 15 231 215<br>1 16 137 191<br>1 12 436 492<br>1 11 310 276<br>1 8 419 404<br>1 7 455 449<br>1 -3 117 122             | $\begin{array}{cccccccccccccccccccccccccccccccccccc$   | 10 -2 125 137<br>10 -4 142 149<br>10 -6 156 169<br>10 -7 432 439<br>10 -9 191 215<br>10-10 186 210                | 7-11 163 165<br>7-12 288 288<br>7-13 193 167<br>8 -6 745 755<br>8 -7 129 162<br>8 -4 141 154                      | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 4 7 136 128<br>4 8 931 880<br>4 14 180 166<br>5 13 467 453<br>5 12 201 210<br>5 10 212 204                    | 3 5 194 207<br>4 14 221 229<br>4 8 153 170<br>4 5 504 667<br>4 3 136 129<br>4 -2 328 281   | 5 -1 186 154<br>6 -3 217 163<br>6 -1 147 135<br>6 1 254 220<br>6 2 255 221<br>6 3 220 204                 | 10 -3 338 355<br>10 -7 200 277<br>11-14 150 95<br>11-12 224 253<br>31 -8 186 173<br>11 -2 456 446               |
| 4 5 205 215<br>4 6 172 163<br>4 0 570 571<br>4 -4 170 163<br>5 -5 215 215<br>4 -3 137 17                       | 1 -5 109 95<br>1 -6 1?7 148<br>1 -7 176 167<br>1 -9 326 320<br>1-10 171 201<br>1-11 198 232                            | 14 -7 107 197 14 -5 198 136 14 -6 286 286 14 -3 447 454 14 -2 145 111 14 5 145 136 14 11 143 132   | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 8 -1 120 132<br>8 2 1001 947<br>8 4 194 206<br>8 5 166 163<br>8 11 265 298<br>8 12 725 709<br>9 11 388 386        | 6 -1 547 542<br>6 -9 315 326<br>6-11 280 771<br>8-15 169 132<br>7-11 279 244<br>7-10 563 543                      | 5 6 127 99<br>5 3 392 405<br>5 2 193 219<br>5 -1 150 124<br>5 -2 223 211<br>5 -3 355 386                      | 4 -4 123 123<br>4 -6 124 115<br>4 -10 678 703<br>5 -11 440 453<br>5 -10 266 271<br>5 -9 272 264  | 6 4 268 253<br>6 5 251 250<br>6 10 185 152<br>6 11 484 507<br>7 15 169 182<br>7 11 209 211<br>7 3 254 24  | 11 0 147 158<br>11 1 178 158<br>11 2 284 283<br>11 4 166 172<br>11 8 394 319<br>11 12 280 275<br>14 156 157     |
| 4-10 344 747<br>4-11 179 152<br>4-12 351 155<br>4-13 237 775<br>4-14 847 872<br>5-15 333 324<br>5-14 55 743    | 2-13 177 166<br>2-11 354 364<br>2-7 314 314<br>2-3 143 151<br>2-1 108 104<br>2 3 590 579                               | 14 13 333 340<br>14 14 167 140<br>15 12 219 215<br>15 4 240 247<br>15 2 275 272<br>15 -2 379 362<br>15 -3 208 210  | 11 7 246 245<br>11 8 652 641<br>11 14 717 708<br>11 15 197 228<br>12 12 264 275<br>12 8 167 181<br>12 7 308 36    | 9 4 129 122<br>9 3 467 449<br>9 1 178 152<br>9 -3 175 217<br>9 -4 289 316<br>9 -5 145 179                         | 7 -6 207 144<br>7 -1 162 176<br>7 0 153 176<br>7 3 144 139<br>7 4 200 211<br>7 5 193 199<br>7 9 136 134           | 5 -7 262 249<br>5 -9 218 244<br>6 -15 310 333<br>6 -13 153 133<br>6 -9 167 150<br>6 -8 137 90<br>6 -7 145 142 | 5 -7 101 203<br>5 -5 105 171<br>5 -4 242 245<br>5 -3 324 323<br>5 -1 165 155<br>5 1 168 168<br>5 3 266 236   | 7 2 653 642<br>7 -6 464 417<br>7 -5 182 181<br>7-14 236 248<br>8-14 256 285<br>8 -6 535 537               | 12 10 170 164<br>12 7 163 136<br>12 6 171 202<br>12 0 312 345<br>12 -4 174 135<br>12 -9 170 169                 |
| 5-12 197 196<br>5-11 325 339<br>5-10 157 155<br>5-9 125 138<br>5-5 576 594<br>5-4 344 353<br>5-1 11 127        | 2 7 422 422<br>2 9 132 89<br>2 10 124 119<br>2 12 216 242<br>2 13 688 627<br>3 11 127 77<br>3 10 132 211               | 15 - 181 196<br>15-12 495 462<br><b>2kl</b><br>J 12 663 652  | 12 6 1086 1060<br>12 5 289 301<br>12 2 185 177<br>12 -6 459 451<br>12 -5 130 93<br>12~13 156 159                  | 9 -9 172 168<br>9-13 332 355<br>9-14 147 172<br>18-15 252 265<br>10-11 146 122<br>10 -6 158 142                   | 7 10 514 464<br>7 14 312 346<br>8 12 539 523<br>8 8 152 163<br>8 2 440 402<br>8 1 175 171                         | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 5 5 265 230<br>5 6 317 313<br>5 8 186 156<br>5 9 347 326<br>5 4 150 139<br>6 3 285 290   | 8 - 4 208 205<br>8 - 204 242<br>8 5 158 150<br>8 10 156 196<br>8 13 181 194<br>8 14 437 452               | 12-10 277 277<br>13 -2 177 229<br>13 -1 344<br>13 5 210 177<br>13 4 221 137<br>13 15 220 242<br>14 0 135 222    |
| 5 1 130 127<br>5 4 367 353<br>5 5 609 594<br>5 9 166 139<br>5 10 154 155<br>5 11 350 379                       | 3 6 131 141<br>3 5 155 123<br>3 -1 103 79<br>3 -2 145 155<br>3 -6 123 143<br>3 -5 271 275<br>3 -5 55                   | 0 8 203 187<br>0 6 972 975<br>0 2 150 158<br>3 0 139 151<br>0 -8 1637 1671<br>0-10 509 528<br>3-12 259 305   | 12-14 274 303<br>12-15 152 145<br>13-15 182 145<br>13-13 367 368<br>13 -9 297 325<br>13 1 542 542<br>13 7 250 228 | 10 -9 278 293<br>10 -3 173 176<br>10 -2 272 266<br>10 8 192 212<br>10 1 365 326<br>10 8 446 425                   | 8 -3 144 166<br>8 -6 152 114<br>9-15 148 158<br>9 -3 -04 416<br>9 -3 170 141<br>9 0 160 152                       | 6 11 634 585<br>7 10 512 494<br>7 9 154 155<br>7 8 146 163<br>7 6 189 162<br>7 2 170 159                      | 0 1 240 247<br>0 -2 221 214<br>5 -3 562 676<br>6 -9 693 712<br>6 -10 198 211<br>5 -13 171 173<br>7 -6 210 194  | 9 9 165 189<br>9 3 142 150<br>9 0 164 166<br>9 -5 406 409<br>9 -6 300 316<br>9 -8 171 234<br>9 -1 145 150 | 14 -1 211 237<br>14 -3 158 127<br>14-11 173 131<br>15 -8 245 269<br>15 -6 162 189<br>15 -2 358 313<br>15 -2 272 |
| 5 12 227 140<br>5 14 387 143<br>5 15 346 378<br>6 13 239 146<br>6 7 315 246<br>6 4 125 99<br>6 1 127 123       | $\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$   | 1-12 263 239<br>1-11 262 269<br>1 -9 233 269<br>1 -8 393 412<br>1 -7 502 527<br>1 -6 165 172   | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 10 4 226 226<br>10 5 209 272<br>11 14 245 230<br>11 4 611 565<br>11 0 272 245<br>11 -2 345 340<br>11 -2 345 340   | 9 1 182 177<br>9 2 191 163<br>9 3 574 568<br>9 6 178 195<br>9 7 411 393<br>9 12 194 166                           | 7 -2 117 99<br>7 -5 239 240<br>7 -6 313 332<br>7 -8 201 197<br>7-10 371 357<br>7-11 369 398<br>7-11 24 24     | 7 1 165 173<br>7 2 148 144<br>7 3 148 154<br>7 4 260 252<br>7 5 391 378<br>7 6 708 691   | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 9kl<br>9-14 648 645   |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$   | 4 -5 137 160<br>4 -6 911 931<br>4 -3 120 140<br>4 6 1255 1232<br>4 10 140 161<br>4 12 244 253<br>5 15 178 170          | 1 1 136 125<br>1 6 228 232<br>1 7 344 336<br>1 8 273 269<br>1 10 152 128<br>1 11 334 324   | 15-12 104 105<br>15-10 364 354<br>15-2 253 259<br>15 0 297 318<br>15 1 159 185                                    | 11 -7 175 192<br>11-13 153 145<br>11-14 123 373<br>12-14 227 225<br>12-12 228 260<br>12 -6 254 275                | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 8-14 159 176<br>8-12 174 202<br>8 -7 136 186<br>8 -6 820 813<br>8 -5 152 172<br>8 -2 229 233<br>8 112 132     | 7 13 169 188<br>8 4 975 943<br>3 -2 170 183<br>5 -6 556 576<br>9 -7 229 224  | 11 2 198 199<br>11 -2 278 297<br>11 -4 230 250<br>11 -8 551 548<br>11 -9 201 218<br>11-12 155 143         | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  |
| 7 - 2 927 910<br>7 - 1 478 433<br>7 1 489 483<br>7 2 345 930<br>7 3 286 930<br>7 3 134 147<br>7 3 134 147      | 5 11 419 421<br>5 10 152 157<br>5 6 151 145<br>5 5 726 716<br>5 4 255 252<br>5 1 133 109<br>5 -3 330 404               | 1 12 167 120<br>1 16 376 369<br>1 15 162 172<br>2 15 162 131<br>2 13 208 166<br>2 9 235 265<br>2 8 129 133   | <b>3ki</b><br>0-14 469 446<br>0-12 915 516<br>0-18 303 384<br>0-8 946 952   | 12 6 175 152<br>13 11 238 231<br>13 7 213 219<br>13 5 123 22<br>13 3 251 258<br>13 -2 166 117                     | 10 -3 203 212<br>10 -4 129 142<br>10 -5 362 350<br>10 -7 238 259<br>10-15 351 336<br>11-10 276 320                | 8 2 352 15A<br>8 4 297 273<br>8 10 151 167<br>9 9 352 35A<br>9 5 156 148<br>9 3 555 543                       | 9-15 200 1AM<br>9-11 354 361<br>9-7 403 429<br>9-2 151 105<br>9-1 470 449<br>9 5 327 316   | $\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$  | 1-12 234 260<br>1-13 206 197<br>1-15 185 196<br>2-13 279 307<br>2-11 155 142<br>2 3 344 364<br>2 7 202 236      |
| 7 13 14 176 177<br>7 14 170 127<br>7 15 145 156<br>7 14 172 145<br>8 10 230 275<br>8 3 154 173                 | 5 -4 179 189<br>5 -5 1169 1251<br>5 -6 524 541<br>5-11 201 234<br>5-13 156 138<br>5-14 169 212                         | 2 5 180 165<br>2 -1 577 589<br>2 -7 922 9%<br>2-10 1% 1%<br>2-11 2%0 186<br>2-12 1%3 108<br>101 1% 1%  | 0 -6 147 165<br>0 -4 662 438<br>0 2 1077 1102<br>0 6 153 156<br>0 8 214 218<br>0 12 411 779                       | 13-3 /59 /67<br>13-11 166 228<br>13-13 255 240<br>14-11 223 217<br>14-10 185 216<br>14 -9 173 163<br>14 3 172 179 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 9 -5 301 314<br>9-14 177 194<br>10-15 319 298<br>10-13 133 252<br>10-11 144 138<br>10 -9 194 199              | 9 8 218 225<br>9 9 457 455<br>10 8 151 155<br>13 7 172 186<br>13 5 256 282<br>10 1 302 333<br>10 $-9$ 190 208  | 14 -7 157 153<br>14 -6 192 208<br>14 6 256 276<br>14 5 198 203<br>15 12 222 203<br>15 2 496 476           | 2 5 213 240<br>2 9 367 344<br>2 13 258 230<br>3 9 195 240<br>3 8 391 378<br>3 -9 189 201                        |
| 8 2 150 109<br>R 1 -01 197<br>8 0 1943 1*93<br>8 -1 393 197<br>8 -2 161 169<br>8 -1 125 173<br>8-10 211 725    | 6-11 291 302<br>6-8 126 106<br>6-8 126 106<br>6-3 508 513<br>6-1 292 280<br>6 1 109 97                                 | 3-13 162 175<br>3-11 221 246<br>3 -7 145 155<br>3 -6 144 140<br>3 4 136 129<br>3 6 155 150   | 1 13 357 356<br>1 11 257 276<br>1 10 260 219<br>1 6 116 97<br>1 6 416 396<br>1 3 503 485                          | 14 5 165 181<br>14 11 211 219<br>15 14 323 325<br>15 8 222 213<br>15 6 205 224<br>15 3 132 46<br>15 8 219 242     | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 11-14 258 234<br>11-12 242 264<br>11 -3 149 123<br>11 2 212 217<br>11 6 128 42<br>12-10 347 393<br>15-11 419 457   | 8kl<br>15-14 197 209<br>8kl<br>12 197 221   | 4-14 219 178<br>4-8 241 275<br>4-7 184 160<br>5-6 284 294<br>4-5 211 228<br>5-4 199 207                         |
| 8-14 171 145<br>9-15 292 292<br>9-11 255 262<br>9 -1 227 37<br>9 1 225 237<br>9 11 267 762<br>9 15 314 292     | $\begin{array}{cccccccccccccccccccccccccccccccccccc$   | 3 8 550 540<br>3 10 121 114<br>3 14 255 268<br>3 15 274 283<br>4 10 187 186<br>4 9 187 192   | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 15 -16 35-9 362<br>15-18 232 211<br>4kl<br>• 12 769 749   | 12 1 186 177<br>12 0 230 224<br>12 -2 877 348<br>12 -3 265 767<br>12 -5 285 742<br>12 -6 322 341<br>12 -12 55 645 | 10 11 356 362<br>10 12 226 232<br>11 10 487 470<br>11 9 175 175<br>11 8 209 214<br>11 6 170 172               | 13-10 149 172<br>13 -7 274 276<br>13 -5 144 134<br>13 13 186 124<br>14 8 250 251<br>14 7 252 250   | 0 4 254 251<br>0 7 133 110<br>0 0 755 746<br>0 -4 975 1005<br>0-10 223 239<br>0-14 255 317                | • 0 200 192<br>• 6 229 259<br>• 10 379 302<br>5 11 203 178<br>5 5 204 232<br>5 0 162 142<br>5 -5 250 285        |
| 10 11 199 134<br>10 7 412 344<br>10 6 176 140<br>10 3 114 107<br>10 2 185 147<br>10 1 172 178<br>10 3 521 779  | 7 4 160 147<br>7 2 200 192<br>7 -1 208 211<br>7 -2 790 785<br>7 -3 190 160<br>7 -4 125 152<br>7 -10 237 253            | 4 6 1807 1964<br>4 5 276 280<br>4 2 167 148<br>4 -4 825 848<br>4 -5 233 295<br>4 -8 292 297  | 2 -5 743 762<br>2 -5 743 762<br>2 +1 214 194<br>2 1 136 143<br>2 3 288 269<br>2 4 132 126<br>2 5 867 862          | 8 8 436 441<br>8 6 128 94<br>8 4 285 264<br>8 2 1396 1431<br>6 8 227 224<br>9 -2 691 677<br>8 -4 485 479          | 13 -7 185 216<br>13 -3 400 395<br>13 -1 312 309<br>13 3 157 175<br>13 9 159 156<br>14 15 179 195                  | 11 2 377 377<br>11 1 137 98<br>11 0 327 314<br>11 -6 672 571<br>11 -8 151 153<br>11 -10 171 175               | 14 +9 324 315<br>14=10 165 136<br>15 +4 160 147<br>15 2 232 236<br>15 4 198 201<br>15 5 212 244  | 1 - 7 145 165<br>1 - 4 147 167<br>1 - 3 355 369<br>1 - 2 275 366<br>1 - 1 404 390<br>1 - 4 174 135        | 5 -6 149 153<br>5 -7 152 163<br>6 -13 228 223<br>6 -7 361 384<br>6 3 259 271<br>6 7 189 189<br>6 9 253 266      |
| 10 -1 105 17#<br>10 -2 197 157<br>10 -6 173 140<br>10 -1 39% 34%<br>10-11 161 144<br>11 -8 611 625             | 7-11 155 156<br>7-12 560 569<br>7-13 319 341<br>1-10 372 392<br>1-9 220 257<br>8 -4 317 299                            | 6-12 183 178<br>4-14 228 194<br>5-13 240 242<br>5 -9 361 398<br>5 -8 131 94<br>5 -6 286 291<br>5 -5 20 51  | 2 13 217 200<br>2 15 107 201<br>3 5 334 342<br>3 4 711 696<br>3 3 242 285<br>3 0 115 95<br>1 9 179 195            | 8 =8 164 167<br>0-12 184 178<br>1 -7 185 124<br>1 -6 205 190<br>1 -3 432 439<br>1 -3 434 436                      | 14 1 196 194<br>14 0 164 167<br>14 -1 249 285<br>14 -5 192 710<br>14 -6 139 154                                   | 12-10 1/ 0 1/0<br>12-13 150 286<br>12-12 459 501<br>12-11 216 263<br>12 -6 156 167<br>12 -7 326 322           | 7ki  | 1 5 222 198<br>1 12 204 296<br>1 15 197 208<br>2 7 319 321<br>2 2 170 155<br>2 1 142 115<br>2 8 124 23    | 6 13 246 227<br>7 7 195 215<br>7 5 165 146<br>7 -6 357 608<br>7-12 380 605<br>7-13 253 249                      |
| 11 -3 236 233<br>11 -2 284 163<br>11 2 206 163<br>11 3 221 233<br>11 6 164 161<br>11 9 136 150                 | 5 0 499 485<br>6 5 152 165<br>8 6 281 289<br>5 8 152 175<br>5 8 152 175<br>5 9 186 132<br>6 10 856 80%<br>7 15 279 282 | 5 -3 140 135<br>5 1 526 488<br>5 3 208 282<br>5 123 119<br>5 5 209 191<br>5 6 246 238  | 1 - 6 363 357<br>3-11 165 136<br>3-12 255 272<br>3-14 395 610<br>6-15 179 151<br>8-16 625 616                     | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 15-13 448 445<br>15 6 165 275<br>15 7 162 179<br>15 10 439 424<br>15 14 245 329                                   | 12 1 168 148<br>12 7 228 222<br>12 8 415 430<br>13 13 285 247<br>15 10 151 156<br>13 9 284 310<br>15 280 315  | 0 -8 152 163<br>0 -6 784 763<br>0 -4 196 190<br>0 -2 266 203<br>0 0 329 288<br>0 4 319 287   | 2 -1 169 186<br>2 -3 583 600<br>2 -6 153 162<br>2 -7 377 410<br>3-12 213 226<br>3 -2 281 266              | 8-4 158 170<br>8 6 444 490<br>8 8 206 224<br>9 11 317 311<br>9 7 294 312<br>9 6 146 717                         |
| 12 15 150 123<br>12 14 356 389<br>12 8 271 277<br>12 6 252 244<br>12 2 173 164<br>12 1 130 199<br>12 0 518 577 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$   | $\begin{array}{c} 5 & 11 & 129 & 113 \\ 6 & 5 & 306 & 296 \\ 6 & 1 & 632 & 622 \\ 6 & 2 & 388 & 291 \\ 6 & 1 & 155 & 147 \\ 6 & 1 & 257 & 256 \\ 6 & -1 & 876 & 817 \end{array}$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 1 7 255 269<br>1 8 146 136<br>1 9 128 130<br>1 10 382 364<br>1 13 294 380<br>1 16 274 311<br>2 9 167 163          | UKI<br>8-14 205 752<br>0-12 634 609<br>0-10 157 166<br>0 -8 272 273<br>1 -6 832 913                               | 13 -7 328 318<br>13-11 404 411<br>14-12 157 133<br>14 10 212 200<br>15 10 342 324<br>15 0 136 176             | 0 14 456 457<br>1 15 276 103<br>1 3 358 353<br>1 2 530 517<br>1 1 233 225<br>1 -1 175 176  | 3 -1 158 145<br>3 1 258 716<br>3 2 336 299<br>3 8 218 230<br>3 11 253 280<br>3 12 195 218<br>4 12 204 158 | 4 5 165 143<br>9 4 173 164<br>9 1 206 717<br>9-15 223 219<br>10-11 184 142<br>10 2 164 143<br>10 3 163 140      |
| 12 -1 192 199<br>12 -2 135 16<br>12 -6 267 26<br>12 -8 261 277<br>12-16 377 38                                 | 9 9 1 446 445<br>4 4 5 364 393<br>5 9 -9 462 469<br>7 9-10 263 271<br>9 10-15 235 259                                  | 6 -3 120 120<br>6 -4 126 111<br>6 -5 268 266<br>6 -9 188 283<br>6-18 149 183   | 6 6 167 164<br>6 8 309 296<br>9 196 196<br>6 10 178 187<br>6 12 958 531   | 2 5 261 269<br>2 3 196 286<br>2 1 180 178<br>2 1 885 798<br>2 4 110 98  | 0 -2 234 219<br>0 6 417 343<br>0 10 216 231<br>0 12 300 312<br>1 12 208 204                                       | 15 -16 215 190<br>15-10 250 262<br>15-14 220 247  | 1 -2 200 191<br>1 -5 195 190<br>1 -6 185 157<br>1 -7 174 165<br>1 -8 261 225<br>1-12 193 203   | 4 10 420 432<br>4 0 548 526<br>5-15 355 348<br>5 -2 235 296<br>5 -1 346 328<br>5 15 227 207               | 10 6 155 167<br>10 7 188 200<br>10 10 163 139<br>10 11 152 88<br>11 8 319 330<br>11 4 346 758                   |

the crystal structure of a  $Mo_6Ga_{31}$  single crystal has slightly different parameters from those observed with  $MoGa_5$  in powder form.

## Description of the structure and discussion

The most prominent features of this crystal structure are its 28 building blocks. Each Mo atom is surrounded by 10 Ga atoms, forming different MoGa<sub>10</sub> polyhedra of very similar shape and size [Fig. 2(a)]. Such TB<sub>10</sub> polyhedra (T = Transition metal, B = Al, Ga) are common in B-metal-rich transition-metal compounds (Table 5) and represent a compromise between two different tendencies in these structures: the tendency of forming TB<sub>12</sub> icosahedra and of forming TB<sub>8</sub> cubes. In fact these TB<sub>10</sub> polyhedra consist of exactly one half of an icosahedron and one half of a cube, reflecting exactly therefore the 'structure equation':

$$\frac{1}{2}TB_{12} + \frac{1}{2}TB_8 = TB_{10}.$$
 (1)

These building blocks in  $Mo_6Ga_{31}$  are arranged in such a way that the molybdenum atoms at the centres occupy vertices of a cubic lattice that is monoclinically distorted. The arrangement of  $TB_x$  polyhedra on a b.c.c. lattice is not uncommon in complex intermetallic phases containing Al or Ga. In fact, the structures of CrGa<sub>4</sub> and MoAl<sub>12</sub> contain building blocks that form



Fig. 2. (a) Coordination polyhedron TB<sub>10</sub> for Mo(1), Mo(2), Mo(3), Mo(4), Mo(5) and Mo(6). (b) Coordination polyhedron (T, B)B<sub>12</sub> for Ga(26).

precisely a b.c.c. structure. In the case of  $CrGa_4$  the building blocks are simple Ga cubes, centred on Cr, and in MoAl<sub>12</sub> the building blocks are Al icosahedra, centred on Mo atoms. The same structural principle may be found in even larger structures like  $Mg_{32}(Zn,Al)_{49}$  (Bergman, Waugh & Pauling, 1957), where complex arrangements of Friauf polyhedra of composition  $T_xB_{113-x}$  also occupy the sites of a b.c.c. lattice.

## Table 5. List of structure types of intermetallic compounds containing $TB_{8}$ , $TB_{10}$ and $TB_{12}$ polyhedra

(T = transition metal, B = A1, Ga.)

Excellent drawings of many of these structure types can be found in Schubert (1964) and Pearson (1972). Only undistorted TB<sub>8</sub> and TB<sub>10</sub> polyhedra are included. Many TB compounds exist with twisted TB<sub>8</sub> coordination like that in CuAl<sub>2</sub> related structures, or in Pt<sub>3</sub>Ga<sub>7</sub> (Ru<sub>3</sub>Su<sub>7</sub> type) or in Ni<sub>2</sub>Al<sub>3</sub>. Distorted TB<sub>10</sub> polyhedra also occur, like those in V<sub>2</sub>Ga<sub>5</sub> (Mn<sub>2</sub>Hg<sub>5</sub> type).

| $TB_8$   |   |  |  |  |  |  |
|--|---|--|--|--|--|--|
| CrGa4<br>Mo3Al8<br>Ti2Ga3<br>Ni3Ga4  | Schubert <i>et al.</i> (1960 <i>a, b</i> )<br>Pötzschke & Schubert (1962 <i>a</i> )<br>Pötzschke & Schubert (1962 <i>b</i> )<br>Ellner <i>et al.</i> (1969) |  |  |  |  |  |
| $Os_2Al_3$   | Edshammar (1965)  |  |  |  |  |  |
| PtAl <sub>2</sub>  | Schubert (1964)   |  |  |  |  |  |
| $TB_{10}$ $Mn_4Al_{11}$ $MnAl_6$ $WAl_4$ $FeAl_3$ $Pt_8Al_{21}$ $Fe_2Al_5$ $Me_3Ce2$ | Bland (1958)<br>Nicol (1953)<br>Bland & Clark (1958)<br>Black (1955)<br>Edshammar (1966)<br>Schubert & Kluge (1953)<br>This work                            |  |  |  |  |  |
| TB <sub>12</sub>   |   |  |  |  |  |  |
| MoAl <sub>12</sub><br>VAl <sub>10</sub><br>V <sub>7</sub> Al <sub>45</sub>           | Adam & Rich (1954)<br>Brown (1957)<br>Brown (1959)  |  |  |  |  |  |

In the case of MoGa<sub>5</sub>, however, there exists a peculiar singularity among the MoGa<sub>10</sub> polyhedra: one polyhedron [Fig. 2(b)] is distorted to such an extent



Fig. 3. Stereo drawing of Mo<sub>6</sub>Ga<sub>31</sub>. The centre atom Ga(26) of the TB<sub>12</sub> polyhedron is marked by an asterisk.

that two more Ga atoms join the shell surrounding the centre atom. In this polyhedron the centre atom is 12-fold coordinated and the atoms are approximately cubic close packed. It is the same polyhedron that has probably a gallium atom at its centre, replacing the expected Mo atom and offering some explanation for the domain of homogeneity in the MoGa<sub>5</sub> phase. Another structural feature worth mentioning is well developed layers consisting of squares of Ga atoms. They form in many different directions but do not penetrate the entire unit cell, as can be seen in the stereo drawing in Fig. 3, made using the computer program of Johnson (1965). It is interesting to see how these Ga layers themselves build up cages containing several MoGa<sub>10</sub> polyhedra.

All these features, but especially the very tightly packed Ga cages around the Mo atoms, can be useful in the interpretation of the anomalous magnetic behaviour of this superconductor. They may also give some clue to the interpretation of the curious behaviour of the melt at temperatures close to the solidification point. In fact it is quite conceivable that  $MoGa_{10}$ clusters form already in the liquid and that the change to the lower coordination number decreases the density of the melt. X-ray diffraction on the melt should allow this point to be clarified.

#### Interatomic distances in Mo<sub>6</sub>Ga<sub>31</sub>

The interatomic distances for the seven independent building blocks of  $Mo_6Ga_{31}$  are listed in Table 3 [computer program: *ORFFE3*, Busing *et al.* (1971*a*)].

The most striking result is the fact that this structure, like many other complex alloy structures, does not exhibit characteristic values for interatomic distances. On the contrary,  $Mo_6Ga_{31}$  shows a great variety of next-neighbour distances, ranging from 2.54 to 2.93 Å for Mo-Ga bonds and from 2.66 to 3.35 Å for Ga-Ga contacts. Although these variations are quite important, one nevertheless finds certain 'mean values' remaining remarkably constant. This is especially true for the mean value of the Mo-Ga distances within one polyhedron whose observed value is around 2.63 (2) Å for all MoGa<sub>10</sub> polyhedra in the structure. It is interesting, therefore, to try to compare this value with the one predicted by the resonating valence-bond theory (Pauling, 1951, 1960).

The relation

$$r_{(1)} - r_{(n)} = 0.30 \log n \tag{2}$$

allows one to correct the single-bond metallic radii for their respective bond number n in intermetallic compounds. In order to do this, one assumes that the electronic structure of the compound is closely similar to the structure of the two metals and one makes some assumptions about the valency of the ligand atoms. If one assumes molybdenum to have a valency of 6 in Mo<sub>6</sub>Ga<sub>31</sub>, the 10 gallium ligands have bond number  $n=\frac{2}{5}$ . The correction,  $-0.6 \log \frac{2}{5}$ , is therefore equal to 0.133. This gives a total predicted bond distance of 2.674 Å for the Mo–Ga distances.\* This value is higher than the observed mean value of 2.63 Å.

If one assigns molybdenum a valency of 7, one obtains 2.634 Å as a predicted value, which comes very close to the experimental value. This should not be interpreted, however, as supporting a valency of 7 for Mo in this compound. More likely is an electron transfer affecting the Mo-Ga distances. Present X-ray data do not permit one to detect such a transfer, although refinement of the occupancy factors (Table 2) seems to indicate that Mo may be an electron *donor*. This would contradict Raynor's hypothesis, transition metals *absorbing* electrons in aluminides (Pratt & Raynor, 1951).

The Ga–Ga distances are systematically longer than those between Mo and Ga or those observed in pure gallium. They vary over an even wider range, and no attempt was made to apply formula (2). It seems very unlikely at the moment that any theory of chemical bonding allows one to predict from first principles variations in interatomic distances of this magnitude, let alone other structural details of  $Mo_6Ga_{31}$ .

The author thanks Professor E. Parthé for his interest and stimulating criticism as well as Professor M. Peter for initiating this study.

\* 
$$r_{Ga} = 1.245, r_{Mo} = 1.296$$
 Å.

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## A Contribution to the Sm–Co Phase Diagram

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The Co-rich part of the Sm-Co system has been investigated by X-ray diffraction, metallographic and thermoanalytic methods. The existence of five closely related compounds ( $Sm_2Co_7$ ,  $SmCo_{5-x}$ ,  $SmCo_5$ ,  $SmCo_{5+x}$  and  $Sm_2Co_{17}$ ) has been confirmed. A tentative phase diagram of the Co-rich part of the Sm-Co system is presented. The practical difficulties encountered in the construction of this phase diagram are discussed.

#### Introduction

Since the discovery that permanent magnets with large coercivity, remanence and energy-product can be prepared on the basis of the SmCo<sub>5</sub> intermetallic compounds, many versions of the phase diagram of the binary Sm-Co system have been presented (Lihl, Ehald, Kirchmayr & Wolf, 1969; Buschow & Van der Goot, 1968; Naastepad, Den Broeder & Klein-Wassink, 1973). Recently, however, two new phases,  $SmCo_{5-x}$  (a phase variant of the CaCu<sub>5</sub>-type structure) (Khan & Feldmann, 1973) and  $SmCo_{5+x}$  (of the TbCu<sub>7</sub>type structure) (Khan, 1974), have been reported to exist in this binary system. Even in the most recent phase diagram of the Sm-Co system (Buschow & Den Broeder, 1973), these two phases are missing. Investigations were therefore carried out in order to amend the Sm-Co phase diagram.

#### Experimental

The alloys in the composition-range  $\text{Sm}_2\text{Co}_7$  to  $\text{Sm}_2\text{Co}_{17}$  were prepared in two series. For the first series, the alloys (1–3 g) were arc-melted on a water-cooled copper hearth under an atmosphere of specially purified argon gas (10–15 ppm oxygen). The elements were supplied by HEK (Lübeck) and had the reported purity 99.9 and 99.999 wt.% for Sm and Co respectively. The second series of alloys was prepared by casting the Sm–Co alloys (weighting about 100–150 g) in copper dies cooled by liquid nitrogen in a Balzer's medium frequency induction oven. The elements for this series were supplied by Th. Goldschmidt (Essen) and had the purity of 99.9 wt.% for both the elements.

The alloys were investigated in the as-cast state as well as after annealing at temperatures between 500 and 1400 °C (depending upon the composition of the alloy)