error so introduced is small. It is possible, since there is a considerable difference in ductility between Zr_4Si and Zr_2Si, that the minor constituent may have been separated preferentially by the filing process.

Although the exact location of Zr_2Si in the constitution diagram was not determined, 'lever rule' considerations would indicate that this intermediate phase must exist over a narrow range of composition near the ideal chemical composition. This is in agreement with the observations of Lundin and coworkers. Lattice parameter measurements of Zr_2Si in the adjacent zirconium-rich and silicon-rich two-phase regions, wherein cell constants should remain invariant, do not show a change in cell dimensions within the accuracy of the measurements, thus adding credence to the previous observation.

The crystal-structure type reported for Zr_2Si by Schachner et al. (1953) is in agreement with the author's results; differences in the positional parameter of the zirconium atoms, about 1/100th of the cell edge, are to be understood since the previous investigators used qualitative intensity measurements. Part of the large discrepancy in lattice parameters can be attributed to the method of specimen preparation; the high chemical reactivity of zirconium makes it unwise to compare data from alloys which were sintered with data from similar alloys prepared by the electric arc–inert atmosphere method used in this investigation. Other influencing factors, such as the sintering atmosphere, crucible material, homogenization procedure, and type of zirconium metal which was used, are not discussed

in sufficient detail by Schachner and coworkers to warrant a comparison of lattice parameters.

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On the Structure of the Heteropoly Anion in Ammonium 9-Molybdomanganate, $(NH_4)_6MnMo_9O_{32} . 8H_2O$.*

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A structure proposed for the complex anion in the heteropoly salt ammonium 9-molybdomanganate, $(NH_4)_6MnMo_9O_{32} . 8H_2O$, has been verified by use of single-crystal X-ray diffraction data. The rhombohedral crystal has space group D_3^7-R32, $a_{rh.} = 10 \cdot 08 \pm 0 \cdot 01$ Å, $\alpha = 104° 24' \pm 3'$. Approximate positional parameters have been determined.

Introduction

The molybdomanganates have been extensively investigated by Friedheim & Samuelson (1900) and Rosenheim (1920), and more recently by Schaal & Souchay (1949). As is the case with most heteropoly

salts, these compounds are stable and very soluble, and crystallize well from aqueous solutions. On making a survey of the crystallography of the heteropoly molybdates, we decided to investigate ammonium 9-molybdomanganate, as a representative of the important series of 9-compounds, which on Rosenheim's classification are intermediate between the two limiting series of 6-compounds and 12-compounds.

Schaal & Souchay have shown that quadrivalent manganese is present in the 9-molybdo complexes, and that their composition corresponds to the presence of the anion $[MnMo_9O_{32}]^{6-}$.

Preparation and analysis

Ammonium 9-molybdomanganate is readily prepared by saturating a boiling solution of alkali paramolybdate with sufficient manganous sulfate to provide enough mineral acid on hydrolysis to convert all of the paramolybdate ions, $Mo_7O_{24}^{6-}$, to metamolybdate, $Mo_4O_{13}^{2-}$. The saturation is carried out in the presence of an oxidizing agent such as ammonium persulfate. Bright orange-red rhombohedral crystals of the salt crystallize out of the solution, and they may be further recrystallized from water. Analysis indicates the composition to be $(NH_4)_6MnMo_9O_{32}.8H_2O$. The experimentally determined density is 3.010 g.cm.$^{-3}$.

Symmetry, unit cell, and space group

The rhombohedral crystals of this salt display Laue symmetry $\bar{3}m$. Some of them exhibit the non-centrosymmetrical face development shown in Fig. 1. It
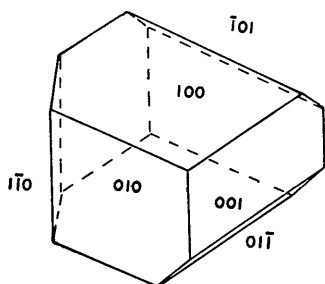

Fig. 1. Crystal of ammonium 9-molybdomanganate showing non-centrosymmetrical face development.

is interesting to note that all of the crystals which show this non-centrosymmetrical face development are of the same enantiomorphic species, although prepared from optically inactive reagents. Moreover, the crystals are strongly piezo-electric, and therefore have no symmetry center. Hence one of the $\bar{3}$ space groups is indicated. The rhombohedral cell edge measured from powder photographs is found to be 10.08 ± 0.01 Å, with the rhombohedral angle $104° 24'\pm3'$. The dimensions of the corresponding hexagonal unit cell are

$$a = 15.94\pm0.01 \text{ Å}, \ c = 12.38\pm0.01 \text{ Å} ,$$

with $c/a = 0.776$. Indexing of Weissenberg photographs obtained on rotation around the threefold axis indicated no systematic absences of any class of reflections, when indices were assigned on the rhombohedral system. The space group is $D_3^7\text{-}R32$. Only one formula unit is contained in the rhombohedral unit cell; the calculated density is 3.076 g.cm.$^{-3}$.

Intensity measurements

Copper $K\alpha$ radiation ($\lambda = 1.542$ Å) filtered through nickel foil was employed to record the intensity data. The multiple-film technique of Robertson (1943) was used and intensities were estimated visually by reference to timed exposures of a strong reflection. An approximately equi-dimensional crystal of about $\frac{1}{2}$ mm. edge was used, and only those reflections occurring on the zero level of the reciprocal lattice were taken into consideration in testing the proposed structure. The Weissenberg photographs were indexed on the basis of both rhombohedral and hexagonal axes.

Description of the structure

A non-centrosymmetrical structure for the 9-molybdomanganate anion consistent with our observations may be described as follows. As there is only one formula unit, $[MnMo_9O_{32}]^{6-}$, in the unit cell the complex must lie on the threefold axis. Also, as there are two oxygen atoms above a multiple of three, these two oxygen atoms must be located on the threefold axis. The postulated structure is built around a manganese atom that is octahedrally surrounded by oxygen atoms. On the same level with this MnO_6 group of atoms are three other octahedral groups centered on molybdenum atoms, each of the three MoO_6 octahedra sharing one of their edges with three non-adjacent edges of the central MnO_6 octahedron. Above and below this middle layer of four octahedra are groups of three MoO_6 octahedra. In each of those groups the three MoO_6 octahedra have one vertex in common, and each octahedron of the group shares two adjacent edges with the other two octahedra. The two groups of three octahedra are placed above and below the middle layer of four octahedra in such a manner that six oxygen atoms in the next plane inwards from each unique oxygen atom on the threefold axis coincide with six oxygen atoms belonging to the middle layer of octahedra. Thus the complete aggregate, consisting of ten joined octahedra, the central one being an MnO_6 octahedron, has the formula $MnMo_9O_{32}$. In addition to the threefold axis through the central manganese atom there are three twofold polar axes, but no symmetry planes or center of symmetry. Approximate coordinates for the manganese atom, the nine molyb-

Table 1. *Atomic coordinates*

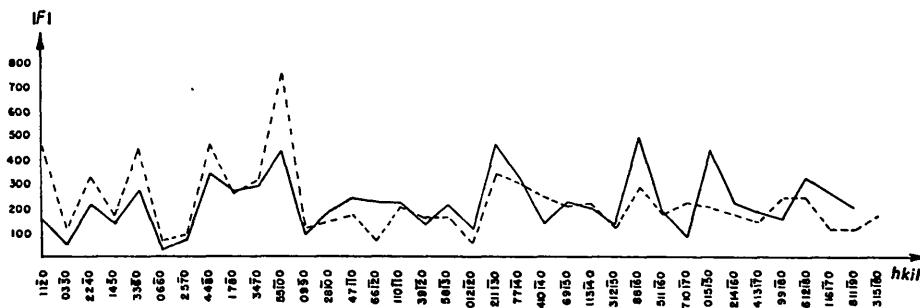| Position	Kind of atom	Coordinates of typical atom (hexagonal axes)		
3(a)	Manganese	0	0	0
9(d)	Molybdenum	0.209	0	0
18(f)	Molybdenum	0.150	0.093	z_1
18(f)	Oxygen	0.113	0.043	z_2
18(f)	Oxygen	0.254	0.114	z_2'
18(f)	Oxygen	0.294	0.041	z_2''
18(f)	Oxygen	0.209	0.000	z_3
18(f)	Oxygen	−0.193	0.000	z_3'
6(c)	Oxygen	0	0	z_3''

Fig. 2. Comparison of observed (full line) and calculated (broken line) structure factors.

denum atoms, and the thirty-two oxygen atoms were calculated for this postulated structure, with inter-atomic distances and positional parameters chosen in accordance with the normal single-bond radii of the atoms concerned. With the notation of the *International Tables* (1935) the assumed positions of the constituent atoms are as shown in Table 1. The numerical values of the z coordinates are not involved in the calculation of the $hki0$ structure factors, and have not been checked. Approximately,

$$z_2 = z_2' = z_2'' = \tfrac{1}{2}z_1 \quad \text{and} \quad z_3 = z_3' = z_3'' = \tfrac{3}{2}z_1 .$$

Discussion

With hexagonal coordinates and indices, the structure factors for the $hki0$ reflections were calculated. The agreement between those calculated values and the observed structure amplitudes is shown in Fig. 2. Although only very approximate corrections have been applied to the observed intensities for scale, temperature and absorption factors, and although the

Fig. 3. The structure of the $[MnMo_9O_{32}]^{6-}$ anion; it is composed of octahedra of oxygen atoms with a metal atom in the center of each octahedron. Left: an exploded view of the ion, showing the three layers of octahedra. The double circle is manganese and the single circles are molybdenum. Right: the oxygen framework of the ion as a whole (metal atoms omitted), showing how the three layers are joined by the sharing of twelve oxygen atoms.

ammonium ions and water molecules have been omitted from consideration, the agreement between the observed and calculated structure factors is sufficiently good to establish reasonably well the correctness of the proposed structure of the anion, which is shown diagrammatically in Fig. 3. Further refinement by Fourier and least-squares procedures is contemplated, and a detailed report will be published later.

The nine molybdenum atoms in the anion may be divided into two groups: the three atoms of the first kind are arranged at the vertices of a triangle coplanar with the central manganese atom, and the six molybdenum atoms of the second kind are arranged in groups of three in planes above and below the middle layer. There are six kinds of oxygen atoms. The first kind, six in number, consists of the oxygen atoms arranged octahedrally around the manganese atom. Each forms a two-thirds bond with manganese, a one-third bond with molybdenum of the first kind and two half-bonds with molybdenum of the second kind. The six oxygen atoms of the second kind are in the same basal plane as those of the first kind. Each forms a single bond with a molybdenum atom of the first kind and a single bond with a molybdenum atom of the second kind. Six oxygens of the third kind also lie in the same basal planes. Each of them forms a one and two-thirds bond with a molybdenum atom of the first kind. There are six oxygen atoms of the fourth kind and six of the fifth kind; they are similarly related to molybdenum and lie in the topmost and bottommost planes of the complex. Each is bonded to a single molybdenum atom of the second kind, by a one and two-thirds bond. There are two oxygen atoms of the sixth kind, each of which forms three two-thirds bonds with molybdenum atoms of the second kind. Thus each molybdenum atom divides its total valence of six in the following way: Mo_1, two one and two-thirds bonds to O_3, two single bonds to O_2 and two one-third bonds to O_1; Mo_2, two one and two-thirds bonds to O_4 or O_5, one single bond to O_2 and one two-thirds bond to O_6 and two one-half bonds to O_1. Fourteen of the oxygen atoms form bonds with bond numbers summing to two, whereas eighteen form bonds (in each case one and two-thirds bonds) with bond numbers deficient by one-third. The total
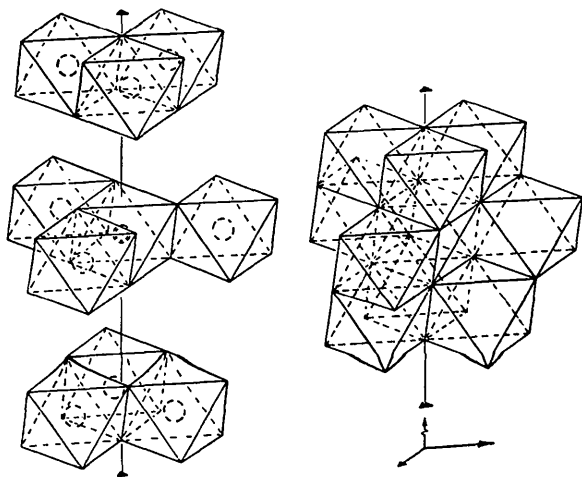
deficiency of one-third of eighteen, namely six, represents the six negative charges on the complex anion.

This structure, like that of the 6-heteropoly compounds, involves octahedral coordination of oxygen atoms around the central ion, whereas the structure of the upper limiting series of 12-compounds and the structure recently published by Dawson (1953) for the more highly condensed 18-anions or doubled 9-anions is based on tetrahedral coordination of the central ion.

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The Crystal Structure of Rhodium Silicide, RhSi

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Rhodium–silicon melts containing between 50 and 75 atomic % silicon when quenched give only two phases: RhSi and Si. The RhSi has the FeSi structure, $B20$ of the *Strukturbericht*, with space group $P2_13$ and $a_0 = 4.675 \pm 0.001$ Å. Four rhodium atoms and four silicon atoms are in positions $(x, x, x;\ x+\frac{1}{2}, \frac{1}{2}-x, \bar{x};\ \bigcirc)$. The parameters, $x_{Rh} = 0.144 \pm 0.003$ and $x_{Si} = 0.840 \pm 0.007$, were determined by trial and error.

There is a real difference between the rhodium parameter in RhSi and the Fe parameter in FeSi but the uncertainty in the Si parameter is such as not to rule out the assignment of bond numbers, as done by Pauling & Soldate in the FeSi case.

Introduction

The melts discussed in this paper were prepared by B. T. Matthias and E. Corenzwit as part of a program of investigation of superconductivity in intermetallic compounds (Matthias, 1952, 1953). Mixtures of rhodium and silicon were put into magnesia crucibles and heated by induction in a helium atmosphere to about $1600 \pm 200°$ C. for a few minutes. The temperature of the melts dropped rapidly when heating was discontinued. Melts with 50, 56, 60, 67 and 75 atomic % silicon were prepared. Matthias found that none of these contained material that was superconducting above $1.3°$ K.*

Determination of the structure

Interpretation of powder photographs of the five melts indicated that two phases (silicon and one with a primitive cubic unit) existed in the melts. The photograph of the 50% melt showed in addition faint lines from a phase which was richer in rhodium. A comparison

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* Private communication.

of the powder pattern of the primitive cubic unit material with tabulated diffraction patterns (Frevel, 1942) suggested isomorphism with the FeSi structure (Phragmén, 1923; Wever & Moeller, 1930; Borèn, 1933; Pauling & Soldate, 1948) and single-crystal work subsequently confirmed this.

A fragment of dimensions $0.08 \times 0.08 \times 0.55$ mm. which was very nearly a single crystal was aligned by the Hendershot (1937) method. Weissenberg photographs were taken using Mo $K\alpha$ radiation. The longest exposure given the zero level was 18 hr. Three simultaneous photographs were taken. The relative intensities of the $(hk0)$ reflections were estimated visually by comparison with a carefully prepared intensity scale.

The symmetry of the X-ray photographs is that of T_h–$m3$ and reflections of the type $(h00)$, h odd, are absent. The space group uniquely indicated therefore is T^4–$P2_13$. The cubic unit cell has $a_0 = 4.675 \pm 0.001$ Å as measured from the powder diffraction photographs of the 50 atomic % melt. If one assumes four molecules of RhSi per unit cell, the calculated density is 8.5 g.cm.$^{-3}$, in good agreement with the pycnometrically determined density of 8.3 g.cm.$^{-3}$.