

$$p(r) \sim V \rho^2 \exp(-Sr/4V), \quad (50)$$

$$q(t) \sim 2\rho \int_0^\infty \exp\left\{-\frac{S}{4V} V(t^2+z^2)\right\} dz. \quad (51)$$

En remplaçant:  $z/t = \sinh u$  on obtient (Watson, 1952, p. 181):

$$q(t) \sim 2\rho \int_0^\infty t \exp\left(-\frac{St}{4V} \cosh u\right) \cosh u \, du \\ = 2\rho t K_1\left(\frac{St}{4V}\right). \quad (52)$$

L'approximation (52) est valable seulement près de l'origine: on peut donc développer (52) en série de  $St/V$  et retenir seulement le premier terme. On trouve dans Watson (1952, p. 80), l'expression de la série ascendante de  $K_1(z)$ :

$$K_1(z) = \frac{1}{2} z \lg \frac{1,08 \dots}{2} z + \frac{1}{z} + \dots \quad (53)$$

On remplace (53) dans (52), on soustrait  $q(0)$ , et on a finalement

$$q(t) - q(0) = \frac{1}{4} \frac{\rho S}{V} t^2 \lg\left(\frac{1,08 tS}{8 V}\right). \quad (54)$$

La forme de la fonction (54) ne dépend pas du choix (50): on obtient le même résultat en utilisant d'autres fonctions au lieu de (50), pourvu qu'elles respectent les conditions indiquées ci-dessus.

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## The Structure of a New Series of $MBe_{12}$ Compounds

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The crystal structures of  $VBe_{12}$ ,  $NbBe_{12}$ ,  $TaBe_{12}$ ,  $CrBe_{12}$ ,  $WBe_{12}$ ,  $MnBe_{12}$ ,  $FeBe_{12}$  and  $CoBe_{12}$  have been determined from single-crystal data. The crystals are isostructural and the space group is  $I_4/mmm-D_{4h}^7$ , with two molecules per unit cell. The dimensions and calculated densities of the tetragonal unit cells are given.

### Introduction

Structure investigations of intermetallic compounds of the type  $MX_{12}$  and  $MX_{13}$  have usually been quite involved. The  $TiBe_{12}$  (Raeuchle & Rundle, 1952) structure, which is not as yet fully established, and the solution of the  $MoBe_{12}$  structure (Raeuchle & von Batchelder, 1955) interested us in the  $MBe_{12}$ -type compounds in the same and neighboring groups of the periodic table as molybdenum.

The crystal structure of  $MoBe_{12}$  is isomorphous with that of  $ThMn_{12}$  (Florio, Rundle & Snow, 1952);  $CrBe_{12}$ ,  $VBe_{12}$  and  $NbBe_{12}$  have been reported by

Kripiakevich & Glodyshevskii (1955) also to be iso-morphous with  $ThMn_{12}$ . The work of the latter investigation on these three  $MBe_{12}$  compounds was done with powders, while our present findings are based on the examination of single crystals.

### Experimental

All the compounds were obtained by melting metal-beryllium mixtures of approximately 1:15 atomic ratio in a tungsten arc, water-cooled copper-hearth furnace, in a controlled helium atmosphere. Each charge was melted several times to ensure a homogeneous melt. In the vanadium and chromium melts, the melting points of the intermetallic compounds

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formed were appreciably higher (several hundred degrees) than those of the individual components.

Each melt was examined spectrochemically and in no case were injurious amounts of impurities found. Debye-Scherrer powder patterns were obtained from portions of each ingot. Single crystals were obtained by an electrolytic etch in very dilute HCl with the small ingot as the anode. The crystals were in the form of minute needles and those that showed some facial developments were examined.

The lattice constants and space groups for all the compounds reported were determined from single-crystal precession diagrams taken around the  $a_0$  and  $c_0$  axes. All the crystals were tetragonal, and since only the reflection absences characteristic of body centering occurred, the space group is  $I_4/mmm-D_{4h}^{17}$  or a subgroup. The lattice constants for the  $MBe_{12}$  intermetallic compounds, using  $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$ , are recorded in Table I along with the calculated densities.

Table I. Lattice constants for the  $MBe_{12}$  compounds

Compound	$a_0$ (Å)	$c_0$ (Å)	$c/a$	$D_x$ (g.cm. <sup>-3</sup> )
V-A Group				
VBe <sub>12</sub>	7.278 ± 0.005	4.212 ± 0.005	0.579	2.37
NbBe <sub>12</sub>	7.376 ± 0.005	4.258 ± 0.005	0.577	2.88
TaBe <sub>12</sub>	7.334 ± 0.005	4.267 ± 0.005	0.582	4.18
VI-A Group				
CrBe <sub>12</sub>	7.230 ± 0.005	4.173 ± 0.005	0.577	2.44
*MoBe <sub>12</sub>	7.271 ± 0.005	4.234 ± 0.005	0.582	3.02
WBe <sub>12</sub>	7.362 ± 0.005	4.216 ± 0.005	0.573	4.25
MnBe <sub>12</sub>	7.276 ± 0.005	4.256 ± 0.005	0.585	2.40
FeBe <sub>12</sub>	7.253 ± 0.005	4.232 ± 0.005	0.583	2.45
CoBe <sub>12</sub>	7.237 ± 0.005	4.249 ± 0.005	0.587	2.49

\* Raeuchle & von Batchelder, 1955.

### Discussion

All of the  $MBe_{12}$  type compounds examined are isostructural with  $MoBe_{12}$ , whose structure has been determined by Raeuchle & von Batchelder (1955).

Edwards & Johnstone (1955-6) in their study of the Cr-Be system reported finding a considerable amount of a second phase  $X$  in the microscopic examination of an alloy containing 71 atomic% beryllium. This unknown phase  $X$  is probably the  $CrBe_{12}$  compound reported here.

The Debye-Scherrer patterns obtained from the melts were essentially single phase and could be indexed as tetragonal  $MBe_{12}$ ; additional phases, however, were present in the  $FeBe_{12}$ ,  $CoBe_{12}$  and  $WBe_{12}$  melts. Considerable work has been reported by others on the Be-Fe system. The first published work was that of Oesterheld (1916), and the latest by Teitel & Cohen (1949) was a study of the equilibrium diagram, in which they found a compound between 7.8 and 8.2

atomic% iron and called it the  $\zeta$  phase with the formula  $FeBe_{11}$  or possible  $FeBe_{12}$ . They indexed all of the diffraction lines from this phase on the basis of a hexagonal cell, so, in order to account for their measured density (2.50 g.cm.<sup>-3</sup>), they found it necessary to assume that there were 1.5 formula weights per unit cell.

It now seems reasonable to assume that the  $\zeta$  phase of Teitel & Cohen (1949) is identical with the tetragonal  $FeBe_{12}$  reported in Table I, since the calculated density (2.45 g.cm.<sup>-3</sup>) of the  $FeBe_{12}$  is in good agreement with the measured density of their  $\zeta$  phase. In any event, the diffraction lines from all powder patterns of our Be-Fe melt can be indexed on the basis of a combination of the tetragonal  $FeBe_{12}$  phase and a face-centered cubic phase of  $FeBe_5$  with  $a_0 = 5.869 \text{ \AA}$ . Three separate melts of Be-Fe were made and the powder patterns were identical in each case; single crystals of  $FeBe_{12}$  were obtained and examined from two of these melts.

The Debye-Scherrer pattern of the Be-Co melt was similar to the Be-Fe pattern and the diffraction lines could be indexed on the basis of tetragonal  $CoBe_{12}$  and a face-centered cubic phase which is probably  $CoBe_5$  with  $a_0 = 5.852 \text{ \AA}$ . The powder pattern obtained for the Be-W melt is very complex but certainly contains the pattern of the tetragonal  $WBe_{12}$  phase; a large number of additional lines occur which have not yet been identified.

Our interests have been in the high-beryllium end of the intermetallic compositions studied and, in all the cases reported here, an isostructural compound of type  $MBe_{12}$  has been found. The investigation is being continued in the examination of transition and precious metals, the results of which will be reported at a later date.

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