

CRYSTALLOGRAPHY

A New Structure in the Magnesium-rich Region of the Cerium-Magnesium System

A compound near the CeMg_6 stoichiometric region in the cerium-magnesium system was indexed as cubic from X-ray powder patterns and was claimed to be two phases¹. An examination² of structures of this approximate stoichiometry indicated that this would represent a new structure if it existed; consequently a structure determination using single crystal techniques was undertaken. Although a subsequent report³ utilizing only powder data indicated a more probable hexagonal cell and isomorphism with the $\text{Th}_2\text{Ni}_{17}$ structure, our preliminary single-crystal data lead to a different result.

A preparation of 6 atomic per cent cerium in magnesium was made in a tantalum crucible sealed by welding in an argon atmosphere. The purity of the magnesium was 99.999 per cent and that of the cerium was 99.9 per cent. Melting was accomplished in a rocking furnace which allowed stirring and provided an argon atmosphere around the crucible. A thermocouple well was provided. Thermal analysis indicated the liquidus at about 612° C and a eutectic at about 594° C. By cooling slowly through the range between 612° and 594° it was possible to grow large crystals of the magnesium-rich compound. These large primary crystals are shown along with the eutectic between the compound and magnesium in Fig. 1. The microstructure consisted of approximately half eutectic and half primary crystals. Using a microscope and a needle, 15 mg of pure compound was removed from the surface of the specimen for X-ray work and chemical analysis. A gravity separation in 1,2-dibromoethylene of the finely ground, etched mixture yielded another 85 mg of the compound. During this gravity separation, rotation of the suspended particles was observed in a magnetic field. Magnetic activity was previously observed by Mahn⁴.

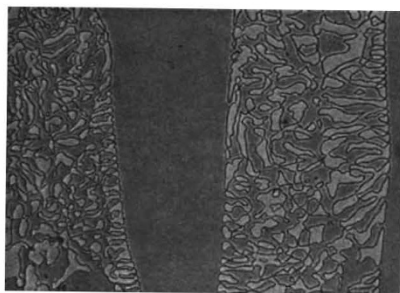


Fig. 1. Microstructure at $\times c. 166$. Etched with 1 part nitric acid, 75 parts glycerol, 24 parts water

Chemical analysis gave 7.94 ± 0.10 atom in per cent cerium for the hand-picked sample and 7.87 ± 0.10 for the gravity-separated sample, corresponding to an approximate stoichiometry of CeMg_{12} .

Nine separate crystals, two or more aligned on each of the three principal axes, were photographed by Weissenberg and precession techniques using both copper and chromium radiation. These crystals were mounted in air since no effect was noticed due to lack of an inert atmosphere. All the diffraction data were consistent with a body-centred orthorhombic cell with $a = b = 10.33 \text{ \AA}$, $c = 77.5 \text{ \AA}$, and $c/a = 13/\sqrt{3}$.

Not only was the size of the cell extraordinary, but also the set of pseudo-extinction rules was most unusual. These rules are given in Table I.

Anticipating some resemblance to the ThMn_{12} structure⁵, due to the c/a ratio and the analytical results, we calculated a three-dimensional Patterson function utilizing the observation that the intensities were approximately

h	k	l
$2n$	$2n$	$26m$
$2n+1$	$2n+1$	$26m \pm 2$
$2n$	$2n+1$	$26m \pm 11$
$2n+1$	$2n$	$26m \pm 13$

equal for reflexions which were permitted and zero for the rest.

In spite of the fact that no data had actually been measured, the results of this Patterson calculation were very rewarding. The positions of the cerium atoms were easily located and are shown in Fig. 2. A reasonable argument can now be put forth regarding the structure. It is postulated that this structure is a stacking of 13 tetragonal ThMn_{12} -type cells with a slip of $y/2$ occurring at $z = 4/26, 10/26, 17/26, \text{ and } 23/26$. Although this represents a new structure, it has a counterpart in the structure proposed⁶ for CuAuII . This structure is formed by stacking 10 $L1_0$ unit cells with a slip of $x/2, y/2$ occurring at $z = 5/10$.

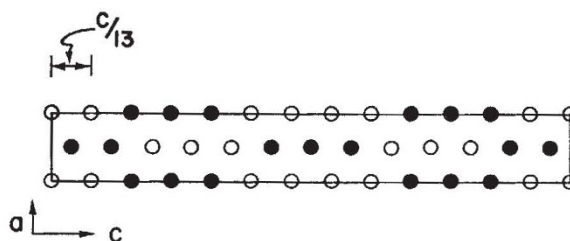


Fig. 2. Unit cell and cerium atom positions of CeMg_{12} . \circ , Cerium at $y = 0$; \bullet , cerium at $y = \frac{1}{2}$

Although some powder patterns in this stoichiometric region are indexable on the basis of the structure described here, other patterns must be indexed on the basis of the normal tetragonal 1-12 structure with $a = 10.33$ and $c = 10.33/\sqrt{3} \text{ \AA}$. This phase has been observed by Evdokimenko and Kripyakevich in the neodymium-magnesium system. We have not yet been able to confirm or deny the existence of the reported 2-17 phase.

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³ Evdokimenko, V. I., and Kripyakevich, P. I., *Kristallografiya*, **8**, 186 (1963).

⁴ Mahn, F., *Rev. Met.*, **46**, 365 (1940).

⁵ Florio, J. V., Rundle, R. E., and Snow, A. I., *Acta Cryst.*, **5**, 449 (1952).

⁶ Johansson, C. H., and Linde, J. O., *Ann. Phys.*, **25**, 1 (1936).

Crystallization of Birefringent, Pseudocubic Horse Apoferritin with Cesium Chloride

As is well known, ferritin, and its protein moiety, apoferritin, can be readily crystallized in aqueous solutions of cadmium sulphate to yield isotropic (cubic) crystals, most commonly octahedra¹. Platy orthorhombic horse ferritin has been described by Harrison², the material having been crystallized originally with cadmium sulphate. A corresponding orthorhombic form of horse apoferritin had not been found. I wish to report that an anisotropic, pseudocubic form of horse apoferritin can be regularly produced by means of concentrated solutions of caesium chloride.

Horse ferritin (twice crystallized) was obtained from Mann Biochemicals, 136 Liberty Street, New York. This