

71), in the compounds (I) and (II) as a bridge, linking Cu(I) atoms. In the complex (III) the SeCN group is out of the ligand sphere. The bond angles M-Se-CN deviate only slightly from 90° , the bond angles M-N-CSe are close to 180° . The deviations from linearity of the SeCN groups have an average value of 5° .

Neutral molecules (diamines, water) in all above mentioned selenocyanate compounds are bonded only to the Cu(II) atoms. In mixed valence complexes (I) and (II) the Cu(II) atom has square pyramidal coordination. In copper(II) selenocyanate complexes central atoms are surrounded by a distorted octahedron.

The calculated interatomic distances $C_2NO...N(en)$ and $SeCN...N(en)$ suggest the presence of hydrogen bonds.

08.2-19 THE DISTRIBUTION OF Cu ATOMS IN THE STRUCTURE OF Cu_8BiS_5 . By M. Ohmura, N. Yamada, Institute of Materials Science, University of Tsukuba, Sakura, Ibaraki, Japan, and K. Tomooka, Department of Geology, Arizona State University, Tempe, Arizona, U.S.A.

In the chemical studies of mixtures of Cu_2S and Bi_2S_3 , a new compound with a ratio Cu:Bi:S=8:1:5 has been synthesized. The material was examined by X-ray diffraction. The hexagonal cell $a = 23.61 \text{ \AA}$, $c = 13.323 \text{ \AA}$, $P6_322$, contains $12 Cu_{19}Bi_{2.5}S_{12}$. Since the reflections corresponding to $h = 6n$, $k = 6n$, and $l = 2n$ (n is any integer) are stronger than the rest, the structure can be regarded as a modulated structure of the smaller cell: $a' = 3.94 \text{ \AA}$, $c' = 6.66 \text{ \AA}$, $P6_3/mmc$. The structure analysis of the latter (the subcell) revealed that the arrangement of the S and Cu atoms is similar to that in $\beta-Cu_2S$ (Sadanaga et al., Min. Jour. (1965) 4, 275).

The Bi atoms occupy centers of the octahedra of S atoms. The intensity distribution of the reflections around the subcell reflections gives the following feature: the intensity of the inner reflection is stronger than that of the outer ones. If an octahedron is occupied by a Bi atom, the octahedron has a larger scattering power and a larger size than an empty one. The characteristic intensity distribution can therefore be attributed to a 'synchronized' effect of the modulation of the scattering power and the modulation of the size of the octahedron.

08.2-20 THE Eu_2O_3 - ZrO_2 BINARY SYSTEM. By I. F. Ferguson and A. Williams, Springfields Nuclear Power Development Laboratories, United Kingdom Atomic Energy Authority (Northern Division), Preston, PR4 0RR, United Kingdom

An investigation of the europia-zirconia binary system has been made to parallel one already reported for the europia-hafnia system (I. F. Ferguson and (Miss) L. Hammonds (1978) Acta Cryst. A34, S154-S155).

Mixed oxides were prepared as follows. The mixed 'hydroxides' were precipitated by the addition of excess ammonium hydroxide to mixed aqueous solutions containing 0.05 g/ml made up from Specpure zirconyl chloride octahydrate dissolved in dilute hydrochloric acid and Specpure europia dissolved in concentrated Analar nitric acid. Excess ammonia was removed by boiling, while the volume of solution was maintained constant by the addition of demineralised water, the precipitate was filtered off, dried at 110°C , lightly ground, transferred to an alumina boat, heated to 900°C for 10 h in air, then to 1300°C for a further 10 h in air and cooled slowly to room temperature. A portion was then removed for X-ray powder diffraction analysis. The remainder was reheated to 1550°C for 10 h and allowed to cool slowly to room temperature. The resultant mixed oxides were examined using an XDC focussing camera set for pure $CuK\alpha_1$ radiation. A duplicate sample was examined similarly but with added NBS standard silicon as an internal standard. Lattice parameter measurements were made using a Hilger and Watts measuring rule and all computations made using a Fortran version of the program FIRESTAR (G. Astle and I. F. Ferguson (1970) UKAEA Report TRG 1812). All sample compositions were determined by X-ray fluorescence analysis and are correct to ± 1 mole %.

In samples prepared at 1300°C it was found that b.c.c. europia could dissolve up to about 5 mole % zirconia when its cube cell edge, a , decreased to 10.834 \AA . Between 9.6 and 39.8 mole % zirconia a two phase region containing b.c.c. and f.c.c. (pseudofluorite) phases occurred. The cell edge of the f.c.c. phase was about 5.338 \AA .

Between 39.8 and 84.8 mole % zirconia a range of f.c.c. solid solutions existed with cell edges which decreased continuously from 5.331 to 5.165 \AA . However, some evidence was obtained for the existence of ordered structures as reported for the europia-hafnia system (I. F. Ferguson and (Miss) L. Hammonds).

At 89.2 and 90.6 mole % zirconia both the f.c.c. phase and a phase based on tetragonal zirconia, with $a = 5.088 \pm 0.004 \text{ \AA}$, $c = 5.1836 \pm 0.006 \text{ \AA}$, were present. However, at 93.6 mole % zirconia the only phases present were indistinguishable from tetragonal and monoclinic zirconia.

Results obtained on samples heated to 1550°C were essentially the same as those reported above except that there seemed to be a greater tendency for the formation of ordered f.c.c. structures based upon the fluorite lattice. This ordering was evidenced by the same a value occurring in samples which differed in composition by 5 or even 15 mole %. In addition some samples heated at 1550°C displayed faint additional diffraction lines which indicated contamination of the f.c.c. phases by one of two phases characterised by d spacings of 6.1 , 2.39 , 2.00 and 1.76 \AA as well as 3.73 , 2.62 , 2.14 , 1.85 and 1.65 \AA . Time did not allow a full investigation to be made of these 'contaminants' but they were not the H1 and H2 phases reported by Kiparisov et al (S. S. Kiparisov et al (1976) Izvestiya Akad. Nauk SSSR, Neorganicheskie Materialy, 12 (9) 1693-1694).