

08.2-19 TWO TYPES OF NON-STOICHIOMETRIC FLUORITE STRUCTURES. By N.N. Bydanov, L.A. Muradyan, B.A. Maximov, V.B. Alexandrov, B.P. Sobolev, V.I. Simonov, Institute of Crystallography, USSR Academy of Sciences, Moscow, USSR.

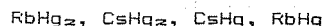
A structural model with a defect normal fluorite ion position ($1/4 \ 1/4 \ 1/4$) and a simultaneous statistic occupation of two interstitial sites on symmetry axes 2, F' ($1/2 \ u \ u$), and 3, F'' ($v \ v \ v$), correspondingly, is thought to be typical of non-stoichiometric phases

$M^{2+}_x R^{3+}_y F^{1-}_{2+x}$ of the fluorite type (sp.gr. $Fm\bar{3}m$). Our neutron-structure investigations of a number of these phases and the analysis of the data published revealed two different structural types of these fluorides. In the first type of structures F' ($1/2 \ u \ u$) ions, $u \approx 0.35-0.37$ occupy statistically interstitial sites on axes 2 only, whereas in the second type F'' ($v \ v \ v$) ions, $v \approx 0.41-0.42$ localize only on axes 3. A structural model with two statistically occupied interstitial sites can be a result of erroneous interpretation of the electron (nuclear) density distribution and a strong correlation of the refined parameters in the least-squares techniques.

The first structural type with interstitial F' ($1/2 \ u \ u$) ion positions is found for: $Ba_{0.73} Pr_{0.27} F_{2.27}$ ($T = 293$ and 573 K); $Sr_{0.84} Lu_{0.16} F_{2.16}$; $Ca_{0.90} Y_{0.10} F_{2.10}$. To the second structural type with additional F'' ($v \ v \ v$) ion positions the following can be safely referred: $Ca_{0.607} Ce_{0.393} F_{2.393}$; $Sr_{0.69} La_{0.31} F_{2.31}$. The type of the structure depended on relations of the ionic radii of R^{3+} and M^{2+} cations. In the first structural type F' ions contact two nearest cations at a distance a little shorter than the $M-F$ one of the corresponding fluorite structure. These structures were recognized at the ratio of ionic radii being $r(R^{3+}) < r(M^{2+})$. Possible cluster models in these two types of structures were discussed. In the 1st type the formation of a cluster occurs as a result of the extraction of 8 atoms from the normal $F(1/4 \ 1/4 \ 1/4)$ ion position, the position on axes 2 being occupied by up to 12 additional $F'(1/2 \ u \ u)$ ions. The vacancy inside this cluster can be occupied by up to 2 additional F ions close to the ($1/2 \ 1/2 \ 1/2$) position, the number of extra $F'(1/2 \ u \ u)$ anions relating to the number of vacancies in the normal position of $F(1/4 \ 1/4 \ 1/4)$ ions as 1.75. In the 2nd type of structures the implantation of 4 $F''(v \ v \ v)$ ions can be a result of the extraction of a single $F(1/4 \ 1/4 \ 1/4)$ ion. The maximum ratio of the number of F'' ions to the number of vacancies of F ions can go up to 4.0. The most likely clusters for the 1st type of structures are M_6X_{26} (8:12:0 - 8 vacancies of F ions; 12 extra F' ions and the absence of F'' ions), M_6X_{27} (8:12:1) and M_6X_{28} (8:12:2). The 2 latter clusters possess 1 or 2 additional F'' ions which are disordered inside the cluster close to the centre of the empty cube ($1/2 \ 1/2 \ 1/2$) of the normal fluorite matrix. The most likely cluster for the structures of the 2nd type is M_4X_{26} (1:0:4) which is smaller in size.

08.3-1 CHEMICAL BONDING BETWEEN CLOSED SHELL ATOMS? STRUCTURAL AND PHYSICAL PROPERTIES OF ALKALI METAL MERCURY COMPOUNDS. H.J. Deiseroth and A. Strunck, Institut für Anorganische Chemie der Universität-GH D-5900 Siegen (FRG)

Recently we reported on preparation conditions and first structural results for the extremely air sensitive mercury compounds of rubidium and cesium (H.J. Deiseroth, A. Strunck, Tenth European Crystallographic meeting Wroclaw (Poland), 1986 Collected abstracts 2C14, p. 252). Up to now we obtained the following mercurides:



Essential structural features of all compounds are characteristic partial mercury lattices with metallic Hg-Hg-contacts ($d=300$ pm). With growing alkali contents an increasing fragmentation of the mercury lattice into smaller clusters takes place. The smallest mercury cluster found up to now is the isolated square planar Hg_4 -group in $CsHg$ ($=Cs_4Hg_4$ see fig.1). It is a most interesting nevertheless open question how bonding between the closed shell mercury atoms in the cluster occurs. Based on structural arguments and physical properties we suggest an intermediate between an ionic $(Cs^+)_4(Hg_4)^{4-}$ and metallic state $(Cs^+)_4(Hg_4)4e^-$ with four free electrons. A comprehensive overview about structure and bonding, the results of further structure determinations and investigations of physical properties will be given.

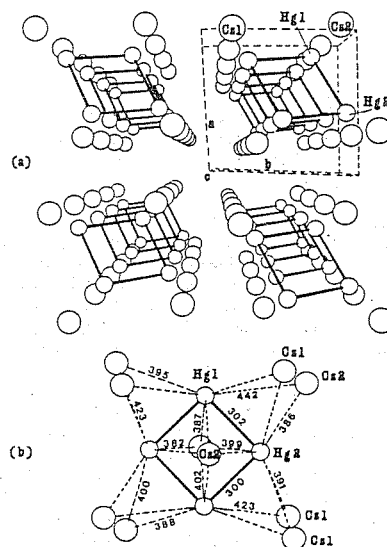


fig.1a: Perspective drawing of the crystal structure of $CsHg$ along $[001]$
fig.1b: One Hg_4 -cluster and its Cs-surrounding viewed approximately along the $[111]$ -direction of the triclinic unit cell (distances in pm, the midpoint of the rectangular Hg_4 -unit is a center of symmetry)