08.2-19   TWO TYPES OF NON-STOICHIOMETRIC FLUO-
RITE 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 fluo-
rite ion position (1/4 1/4 1/4) and a simulta-
neous 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
$M^{2+}_{1-x} R^{3+}_x F^{1-}_{2+x}$ of the fluorite type (sp.gr.Fm3m).
Our neutron-structure investigations of a number
of these phases and the analysis of the data
published revealed two different structural ty-
pes of these fluorides. In the first type of
structures F' (1/2 u u) ions, $u \approx 0.35$-0.37 oc-
cupy 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 occu-
pied interstitial sites can be a result of er-
roneous interpretation of the electron (nucle-
ar) density distribution and a strong correla-
tion 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 struc-
tural type with additional F" (v v v) ion po-
sitions 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 nea-
rest 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 oc-
cupied 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 im-
plantation 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 $M_6 X_{36}$ (8:12:0 - 8 vacancies of
F ions; 12 extra F' ions and the absence of F'"
ions), $M_6 X_{37}$ (8:12:1) and $M_6 X_{38}$ (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 $M_4 X_{26}$ (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:

 $RbHg_2$, $CsHg_2$, $CsHg$, $RbHg$
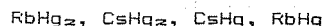
Essential structural features of all
compounds are characteristical partial
mercury lattices with metallic Hg-Hg-contacts
(d=300pm). With growing alkali contents an
increasing fragmentation of the mercury
lattice into smaller clusters takes place.
The smallest mercury cluster found up to now
is the isolated square planar Hg_4-group in
CsHg (=$Cs_4 Hg_4$ 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
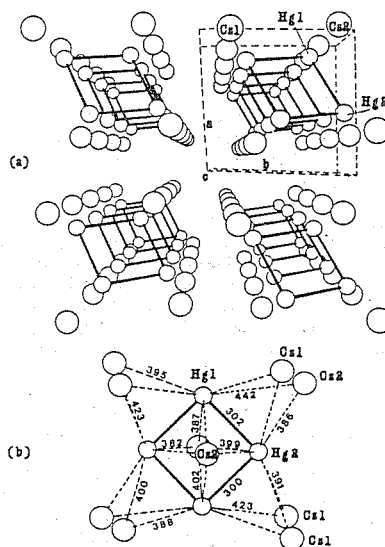properties will be given.

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 mid-
point of the rectangular Hg_4-unit is
a center of symmetry)