Acta Cryst. (1966). **21**, 1012

Crystallographic data for solvated rare earth chlorides.*

By EDWARD J. GRAEBER, GEORGE H. CONRAD and SHERWOOD F. DULIERE, *Sandia Laboratory, Albuquerque, New Mexico, U.S.A.*

(*Received* 4 *August* 1966)

In connection with studies on the luminescence decay times of solvated rare earth chlorides (Freeman, Crosby & Lawson, 1964), an X-ray analysis of $XCl_3.6H_2O$ compounds was undertaken. It is known that the trichloride hexahydrates of neodymium, samarium, erbium (Pabst, 1931; Iveranova, Tarasova & Umanskii, 1951), gadolinium (Marezio, Plettinger & Zachariasen, 1961), and europium (Bel'skii & Struchkov, 1965) form a series of isostructural compounds. The detailed crystal structures of the gadolinium (Marezio, Plettinger & Zachariasen) and europium (Bel'skii & Struchkov) compounds have been reported. Crystals of these compounds possess monoclinic symmetry (space group, $P2/n$) with two molecules per unit cell. We wish to report lattice constants and optical properties on the lanthanide chloride hexahydrates containing cations $Z=62$ to $Z=69$. Further work is not contemplated on these isomorphous compounds.

Single crystals of the trichloride hexahydrate were prepared by dissolving rare earth oxides (Research Chemicals, Inc. 99·9+ %) of samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium and thulium in concentrated solutions of hydrochloric acid in water. The habit (tabular parallel to [010], with prism faces longer than clinodome faces) reported by Pabst for $GdCl_3.6H_2O$ and $SmCl_3.6H_2O$ is displayed by all members of this series.

The crystal data are summarized in Table 1. Cell parameters were determined from precession photographs (Mo $K\alpha$, $\lambda=0{\cdot}7107$ Å); for the samarium, europium, gadolinium and erbium compounds, our values are in satisfactory agreement with those previously reported. Densities were measured on a Berman torsion balance. The optical properties were determined by the immersion method from which the optic sign was observed negative. The crystal orientation observed for the entire series was $Y\|\mathbf{b}$ with no

Table 1. *Crystal data*

Formula	$SmCl_3.6H_2O$	$EuCl_3.6H_2O$	$GdCl_3.6H_2O$	$TbCl_3.6H_2O$	$DyCl_3.6H_2O$	$HoCl_3.6H_2O$	$ErCl_3.6H_2O$	$TmCl_3.6H_2O$
Mol. wt.	364·79	366·40	371·69	373·37	376·94	379·37	381·72	383·38
a (Å)*	9·67	9·68	9·64	9·63	9·61	9·58	9·57	9·55
b (Å)*	6·55	6·53	6·53	6·51	6·49	6·47	6·47	6·45
c (Å)*	7·96	7·96	7·93	7·89	7·87	7·84	7·84	7·82
β*	93° 40′	93° 40′	93° 40′	93° 40′	93° 40′	93° 40′	93° 40′	93° 40′
U (Å^3)	503	502	498	493	490	486	484	481
D_m(g.cm^{-3})*	2·382	2·418	2·468	2·492	2·525	2·564	2·588	2·608
D_x(g.cm^{-3})	2·407	2·423	2·478	2·513	2·554	2·594	2·604	2·617
nx*	(1·570)	1·570	1·572	1·572	(1·574)	1·574	1·574	(1·574)
ny*	(1·578)	1·578	1·580	1·580	(1·580)	1·582	1·582	(1·582)
nz*	(1·582)	1·582	1·584	1·584	(1·586)	1·586	1·586	(1·586)
$2V$	(~60°)	~70°	~75°	~75°	(~75°)	~80°	~80°	(~80–85°)
Bulk color	Yellow	Colorless	Colorless	Colorless	Faintly yellow	Honey yellow	Light pink	Light green

* Estimated probable error values (maximum): 0·015, 0·010, 0·012, 5′, 0·002 for a, b, c, β, D_m respectively and 0·002 for refractive indices. Values in parentheses are from Thoma & Insley (1964)

* This work was supported by the United States Atomic Energy Commission.

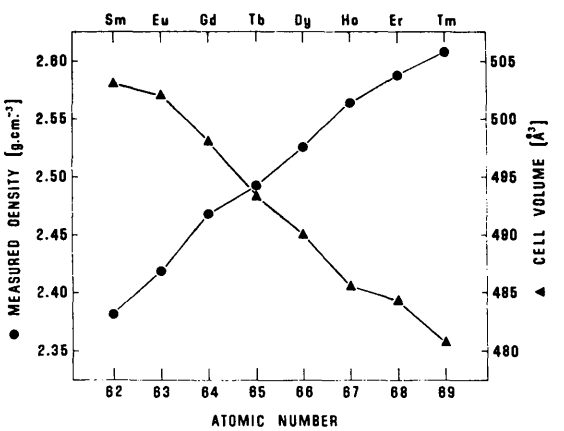

Fig. 1.

perceptible dispersion of the optic axis. In Fig. 1 density and cell volume are plotted *versus* atomic number of cation; the characteristic contraction of the lanthanide series is clearly observed.

References

BEL'SKII, N. K. & STRUCHKOV, YU. T. (1965). *Soviet Phys., Cryst.* **10**, 15.

FREEMAN, J. J., CROSBY, G. A. & LAWSON, K. E. (1964). *J. Mol. Spectr.* **13**, 399.

IVERANOVA, V. I., TARASOVA, V. P. & UMANSKII, M. M. (1951). *Izvest. Akad. Nauk SSSR, Ser. Fiz.* **15**, 164.

MAREZIO, M., PLETTINGER, H. A. & ZACHARIASEN, W. H. (1961). *Acta Cryst.* **14**, 234.

PABST, A. (1931). *Amer. J. Sci.* **22**, 426.

THOMA, R. E. & INSLEY, H. (1964). Private communication.

Acta Cryst. (1966). **21**, 1013

The lattice parameter in the solid solution KCl-KBr.

By O. D. SLAGLE* and H. A. MCKINSTRY, *Materials Research Laboratory, Pennsylvania State University, University Park, Pennsylvania* 16802, *U.S.A.*

(*Received* 20 *November* 1965 *and in revised form* 3 *August* 1966)

The purpose of this investigation was to study the lattice parameter of the solid solution series KCl–KBr and to use the results to define the dependency of the lattice parameter on composition. Arbitrarily, one can propose a variation for the lattice parameter in the form:

$$a_{ss}^n = a_1^n c_1 + a_2^n c_2$$

where a_{ss}, a_1 and a_2 are the lattice parameters in the solid solution, potassium chloride and potassium bromide, respectively, c_1 and c_2 are the respective concentrations (mole fractions) and n is an arbitrary power describing the variation. Vegard (1921) suggested that for many substances $n=1$ while Grimm & Herzfeld (1923) on the basis of theoretical arguments predicted $n=8$. The more recent theoretical investigation of Durham & Hawkins (1951) predicted values of the lattice parameters which are in close agreement with those given by Retger's law of additive volumes, that is $n=3$. The lattice parameter of the solid solution KCl–KBr has previously been measured by Havighurst, Mack & Blake (1925) and Oberlies (1928). In neither case were the data of sufficient accuracy to imply an exponent other than $n=1$.

The polycrystalline samples of the solid solution were prepared by melting. The quenched mixture was ground to 325 mesh and annealed at 500°C for ½ hr. A Picker X-ray diffractometer was used to record the high angle Bragg peaks with Cu $K\alpha$ radiation and scanning at a rate of 0·1°min^{-1} both up and down through each peak. The temperature of the sample was controlled to ±0·1°C. The angle of each peak was determined as the midpoint of the peak at half height. From each measured angle the lattice parameter was determined and plotted against the extrapolation function $\cos^2\theta/\sin\theta$ to remove the systematic errors. Such an analysis indicated that the uncertainty in the lattice parameter was 0·005 %. If the uncertainty in the composition is assumed to be 0·1 %, then one can expect an additional uncertainty in the lattice parameter of 0·005 %. The expected uncertainty is then 0·01 %.

The experimental values of the lattice parameter were used to find the least-squares values of the exponent n.

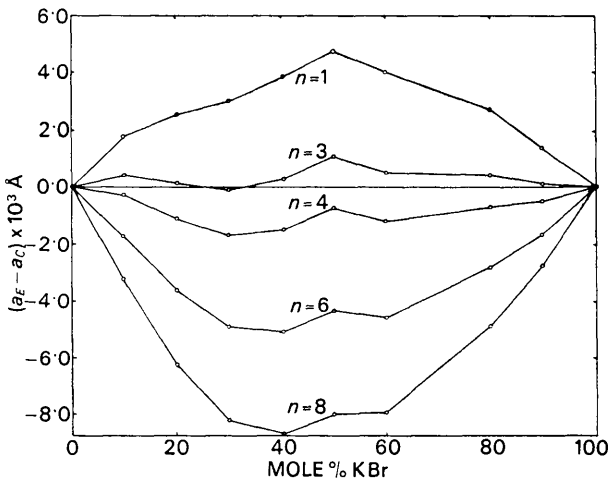

Fig. 1. The difference between the experimental values of the lattice parameter for the crystalline solution KCl–KBr and the values calculated with the use of different values of n, as indicated, is plotted as a function of the mole composition.

The end member lattice parameters at 25·0°C were found to be: a_{KCl} ($c_1=1{\cdot}0$) = 6·2927 Å and a_{KBr} ($c_2=1{\cdot}0$) = 6·5993 Å using Cu $K\alpha_1$ = 1·54051 Å and Cu $K\alpha_2$ = 1·54433 Å.

The differences between experimental and calculated lattice parameters are shown in Fig. 1.

The best fit was obtained for $n=3{\cdot}26$ with a 3σ tolerance of ±0·26. The previously proposed exponential constants of 1 and 8 can thus be rejected for this system and Retger's law of additive volumes may be assumed to hold within experimental error.

References

DURHAM, G. S. & HAWKINS, J. S. (1951). *J. Chem. Phys.* **19**, 149.

GRIMM, H. G. & HERZFELD, K. F. (1923). *Z. Phys.* **16**, 77.

HAVIGHURST, R. J., MACK, E. & BLAKE, F. C. (1925). *J. Amer. Chem. Soc.* **47**, 29.

OBERLIES, F. (1928). *Ann. Phys. Lpz.* **87**, 238.

VEGARD, L. (1921). *Z. Phys.* **5**, 17.

* Present address: Battelle-Northwest, Richland, Washington, U.S.A.