

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., PLETINGER, 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.*

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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<sup>-1</sup> 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  $n$ .

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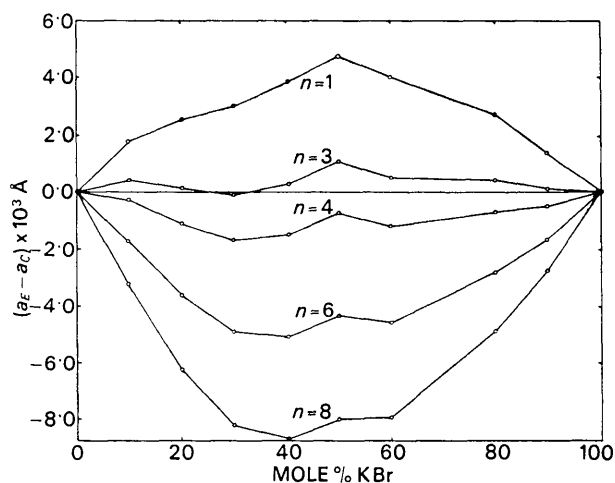


Fig. 1. The difference between the experimental values of the lattice parameter for the crystalline solution KCl-KBr and the values calculated with the use of different values of  $n$ , as indicated, is plotted as a function of the mole composition.

The end member lattice parameters at 25.0°C were found to be:  $a_{\text{KCl}} (c_1=1.0)=6.2927 \text{ \AA}$  and  $a_{\text{KBr}} (c_2=1.0)=6.5993 \text{ \AA}$  using Cu  $K\alpha_1=1.54051 \text{ \AA}$  and Cu  $K\alpha_2=1.54433 \text{ \AA}$ .

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

The best fit was obtained for  $n=3.26$  with a  $3\sigma$  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.