present measurements. The ratio μ_λ/μ_e however, was found to rise from 0·033 to 0·048 with the increased accelerating potential and so the beam homogeneity appears to be substantially independent of tube voltage.

In Table 1 the observed flux changes at 30 kV are compared with those predicted on the basis of (1) for 30 kV and 12 kV for a beam of 1 mm diameter that subtends 16 minutes of arc (0·26°) at the tube focus. The results show that for intensity measurements of 1% accuracy the take-off angle should never be less than about 5° for Cu $K\alpha$ radiation.

References

Alexander, L. E. & Smith, G. S. (1962). *Acta Cryst.* **15**, 983.

Burbank, R. D. (1964). *Acta Cryst.* **17**, 434.

Cole, H., Chambers, H. W. & Wood, C. G. (1962). *Rev. Sci. Instrum.* **33**, 435.

Furnas, T. C. Jr (1957). *Single Crystal Orienter Instruction Manual.* Milwaukee: General Electric Co.

Young, R. A. (1969). *Acta Cryst.* A**25**, 55.

Acta Cryst. (1970). A**26**, 156

Low temperature X-ray investigation of NH_4Br.*

By A. Bonilla,† C. W. Garland and N. E. Schumaker,‡ *Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts* 02139, *U.S.A.*

(*Received* 27 *March* 1969)

The lattice parameters of NH_4Br have been measured as a function of temperature from 5 to 150°K, a range which includes the region of the transition between cubic and tetragonal ordered phases. The low-temperature CsCl-type phase exhibits normal thermal expansion up to ~108°K on warming, while the tetragonal diffraction pattern persists down to ~80°K on cooling. The present data are combined with previous measurements between 150 and 300°K to yield an overall picture of the variations associated with changes in ordering.

Four different structural modifications of NH_4Br are known to exist at low pressures, and a fifth modification of unknown structure has recently been observed above 2000 atm (Garland & Young, 1968). At one atmosphere and high temperatures NH_4Br has a disordered NaCl-type structure, but it undergoes a first-order transition at 410°K to a disordered CsCl-type structure. [Pöyhönen, Mansikka & Heiskanen (1964) have measured the lattice parameters between 297 and 467°K.] This modification undergoes a cooperative λ transition at 234·5°K to an ordered tetragonal structure which is closely related to the CsCl structure (Levy & Peterson, 1953). At lower temperatures there is a sluggish first-order transition to an ordered CsCl-type structure. Associated with this latter phase change is a marked hysteresis: the transition occurs at ~78°K on cooling and at ~108°K on warming (Stephenson & Adams, 1952; Sorai, Suga & Seki, 1965). The order-disorder referred to above involves the relative orientations of adjacent NH_4^+ ions. Below 234·5°K there is a long-range order in these orientations although this ordering will not be the same in the tetragonal and CsCl-type structure.

Hovi, Heiskanen & Varteva (1965) have carried out a detailed X-ray determination of the lattice parameters of NH_4Br as a function of temperature between 150 and 300°K. The object of the present investigation was to confirm the cubic structure of the low-temperature phase, to determine the lattice parameter as a function of temperature, and to investigate by means of X-ray diffraction the region of the order–order transition at ~100°K. To achieve these goals, we have obtained data between 5 and 150°K.

Except for a measurement at 5°K and a reference measurement at 295°K, all data were obtained on a General Electric Model XRD-5 diffractometer using a 'Cryo-tip' temperature regulator with X-ray vacuum shroud. The specimen was a layer of finely ground NH_4Br (Mallinckrodt Analytical Reagent) with a small amount of collodion used as binder and adhesive. Temperatures were measured with a chromel–constantan thermocouple and are accurate to within ±1°K. A Philips diffractometer with liquid helium sample holder was used to obtain data at ~5°K.

Silicon powder (40% by weight) was added to the NH_4Br as an internal standard except for some of the measurements in the ordered cubic phase. A silicon lattice parameter of 5·43097 Å was used at 25°C (Straumanis & Aka, 1952), and values at low temperatures were obtained from the thermal expansion data of Erfling (1942). The instrumental corrections indicated by the Si lines were always quite small: $\Delta(2\theta)\simeq 0{\cdot}17°$ for lines with 2θ values between 70 and 125°. Stronger lines obtained with pure NH_4Br permitted a better determination of the small shifts which occur with temperature below 100°K, and such measurements were also made. Ten high-angle NH_4Br lines – 300+221, 310, 311, 222, 321, 400, 410+322, 411+330, 420, 421 – were used to determine the lattice parameters. The uncertainty in the absolute values of the cubic lattice parameters is ±0·001 Å, and relative values are quite a bit more precise. The errors associated with the a_3 values in the tetragonal phase are greater due to the small separation between the hhl and the hll components of a line and the presence of Cu $K\alpha_1\alpha_2$ splitting.

Fig. 1 shows the variation in the NH_4Br lattice parameters between 0° and 300°K after a correction has been applied to the data of Hovi *et al.* (1965). At 295°K, we obtained 4·0588±0·0006 Å for the lattice parameter of NH_4Br, whereas Hovi *et al.* give a value of 4·0574±0·0005 Å. Since our value is in good agreement with other recent room-temperature values (see Fig. 1), it is probable that all the

---

* This work was supported in part by the Advanced Research Projects Agency.

† Supported by Economic Development Administration of Puerto Rico.

‡ Present address: Bell Telephone Laboratory, Murray Hill, New Jersey.

values reported by Hovi *et al.* are systematically low. Thus, a temperature-independent increment of 0·002 Å has been added to each of Hovi's data points in Fig. 1. In any case, the relative changes which occur near phase transitions are of greater interest than the absolute values. It should be pointed out that the tetragonal unit cell contains two molecules of NH_4Br; the tetragonal axis (of length a_3') is parallel to one of the original cubic axes, while the other two axes (length denoted by $a_1'=a_2'$) lie at a 45° angle with respect to the original cubic axes. Changes in lattice spacing are more clearly represented by retaining the original system of axes. Thus, Fig. 1 shows the values of $a_1=a_2=a_1'/\sqrt{2}$, while both sets of parameters are given in Table 1.

Analysis of the 5°K diffraction pattern definitely confirms that the low-temperature phase has a cubic structure. Moreover, Fig. 1 clearly shows that the thermal expansion in this phase is normal all the way up to the transition at ~108°K. This is in agreement with the heat-capacity variation observed by Sorai, Suga & Seki (1965) and Cole (1952), but differs from the result of a recent infrared investigation by Schumaker & Garland (1969). The infrared spectrum of NH_4Br at 20°K is essentially identical to that of NH_4Cl and consistent with a parallel ordered CsCl-type structure, but new features indicative of a breakdown in the selection rules for T_d symmetry are observed between ~70 and 108°K. The absence of anomalous behavior in the X-ray diffraction pattern suggests that such 'distorted' sites are few in number and probably isolated from each other.

Table 1. *Smooth-curve values of the lattice parameters of* NH_4Br *at* 1 *atm in its various low-temperature modifications*

All values are cited in Ångstrom units.

Disordered CsCl-type

T	$a_1=a_2=a_3$
300°K	4·0596
280	4·0564
260	4·0532
240	4·0500
235	4·0491

Ordered CsCl-type

T	$a_1=a_2=a_3$
108°K	4·0128
100	4·0117
80	4·0084
60	4·0057
40	4·0038
20	4·0026
0	4·0023

Table 1 (*cont.*)

Ordered tetragonal structure

T	$a_1'=a_2'$	a_3'	$a_1=a_2=a_1'/\sqrt{2}$
230°K	5·7284	4·0628	4·0506
220	5·7260	4·0635	4·0490
200	5·7220	4·0634	4·0461
180	5·7180	4·0615	4·0433
160	5·7139	4·0582	4·0404
140	5·7098	4·0540	4·0375
120	5·7057	4·0489	4·0346
108	5·7033	4·0457	4·0329
100	5·7016	4·0435	4·0317
80	5·6972	4·0384	4·0286

Although the intensity variations observed in the low-temperature X-ray patterns are consistent with a CsCl-type structure, there is, of course, no direct X-ray indication of the NH_4^+ ordering. Two facts, in addition to the infrared spectrum at 20°K, strongly indicate parallel ordering as in NH_4Cl. First of all, the analogous phase in ND_4Br is stable up to 165°K and neutron diffraction measurements show that this crystal is parallel ordered at ~77°K (Levy &

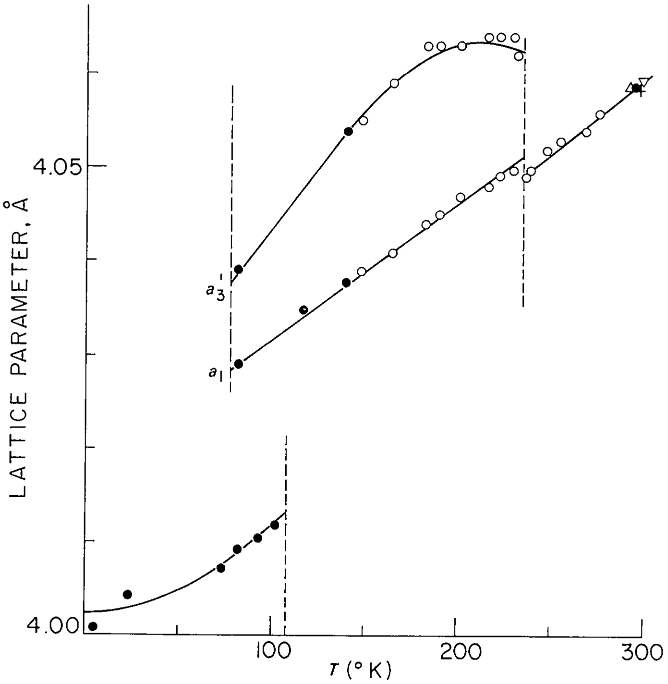

Fig. 1. Lattice parameters of the ordered cubic, ordered tetragonal, and disordered cubic modifications of NH_4Br as a function of temperature. ● present data; ○ data of Hovi, Heiskanen & Varteva (1965) with each value increased by 0·002 Å (see text); △ datum of Deshpande & Sirdesmukh (1961); + datum of Pöyhönen, Mansikka & Heiskanen (1964); ▽ datum of Swanson & Fuyat (1953).

Peterson, 1953). The normal and deuterated bromide have essentially the same lattice parameter at 296°K and Levy & Peterson (1953) cite ~4·00 Å as the *a* value of ND_4Br at 77°K, which is in reasonable agreement with our value of 4·008 Å at that temperature. Secondly, the ratio $R = a(100°K)/a(295°K)$ is almost identical for NH_4Cl and NH_4Br in its cubic phase. The value of *R* obtained from our NH_4Br measurement is $0{\cdot}9882_7$, while the *R* value calculated from the NH_4Cl data of Pilbrow & Spaeth (1967) is $0{\cdot}9881_3$. A more detailed comparison of this sort is not possible since no reliable NH_4Cl lattice parameters have been reported below 100°K.

The authors wish to thank Dr R. A. Young, now at Data Acquisition and Control Systems Center of IBM, for making the liquid helium measurements. We are especially grateful to Professor D. P. Shoemaker for allowing us the extended use of his General Electric diffractometer.

References

Cole, A. G. (1952). Ph. D. Thesis, Massachusetts Institute of Technology.

Deshpande, V. T. & Sirdesmukh, D. B. (1961). *Acta Cryst.* **14**, 353.

Erfling, H. D. (1942). *Ann. Physik*, **41**, 467.

Garland, C. W. & Young, R. A. (1968). *J. Chem. Phys.* **49**, 5282.

Hovi, V., Heiskanen, K. & Varteva, M. (1965). *Low Temperature Physics* LT9 (Part B), 1179.

Levy, H. A. & Peterson, S. W. (1953). *J. Amer. Chem. Soc.* **75**, 1536.

Pilbrow, J. R. & Spaeth, J. M. (1967). *Phys. Stat. Sol.* **20**, 225.

Pöyhönen, J., Mansikka, K. & Heiskanen, K. (1964). *Ann. Acad. Scient. Fenn.*, Ser. A. **6**, (168), 18.

Schumaker, N. E. & Garland, C. W. (1969). To be published.

Sorai, M., Suga, H. & Seki, S. (1965). *Bull. Chem. Soc. Japan*, **38**, 1125.

Stephenson, C. C. & Adams, H. E. (1952). *J. Chem. Phys.* **20**, 1658.

Straumanis, M. E. & Aka, E. Z. (1952). *J. Appl. Phys.* **23**, 330.

Swanson, H. E. & Fuyat, R. K. (1953). NBS Circular 539, Vol. II, p. 51.

Acta Cryst. (1970). A**26**, 158

The application of some liquid scattering functions to X-ray data from the zeolite complex *m*-dichlorobenzene–Ni-faujasite.

By H. D. Simpson and H. Steinfink, *Materials Science Laboratory, Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas* 78712, *U.S.A.*

(*Received* 8 *April* 1969 *and in revised form* 18 *June* 1969)

The application of formulae for the average scattering of X-rays from *m*-dichlorobenzene molecules and exchangeable nickel cations uniformly distributed in the intracrystalline channels of the zeolite natural faujasite is illustrated. Application of these formulae to the actual X-ray data revealed that the sorbed *m*-dichlorobenzene molecules and previously unlocated nickel cations form a liquid or near liquid in the zeolite channels.

Introduction

During a recent crystal structure analysis of Ni faujasite saturated with *m*-dichlorobenzene and of Mn faujasite saturated with 1-chlorobutane (Simpson & Steinfink, 1969) it became evident that the sorbed molecules form a liquid or near-liquid in the interconnected supercages defined by the aluminosilicate framework. It is known that the centers of these cages are at definite crystallographic sites (Bergerhoff, Baur & Nowaki, 1958; Baur, 1964). The liquid scattering is modified by this periodic arrangement, resulting in a significant contribution by the sorbed guest molecules and unlocated nickel cations to the low order structure factors.

During the course of the analysis of the low order X-ray data for the *m*-dichlorobenzene complex, many models were tried in an effort to elucidate possible preferred orientation and ordering of the guest molecules before it was finally concluded and demonstrated that the best model is one which postulates an essentially uniform distribution of the electron density of these molecules in the channels formed by the supercages. In this paper we present the scattering equations used for the uniformly distributed *m*-dichlorobenzene molecules and nickel cations in some of the trial models and the final model, and the effect of each model on the low order structure factors. Only the *m*-dichlorobenzene complex is considered since the analysis of the 1-chlorobutane complex was very similar.

Before reaching the stage of analysis in which the models presented here were tried, it was established that there were about four molecules of *m*-dichlorobenzene per supercage and that about 0·9 nickel cations were uniformly distributed in each supercage as well as in each sodalite cage. The space group is *Fd*3*m*. The centers of the supercages, the sodalite cages, and the hexagonal prisms (which connect the sodalite cages together) are Wyckoff positions *b*, *a* and *c* respectively, and their respective approximate free dimensions are 12, 7 and 3 Å.

Formulae for the average scattering from atoms distributed uniformly throughout the volume of a sphere and on a circular arc have been given by King & Lipscomb (1953), and the formula for the average scattering from an atom uniformly distributed over the surface of a sphere has been given by Verweel & Bijvoet (1938) and Zachariasen (1945). Derivations and graphical presentations of the modifying functions in some of these formulae are given by James (1950).

The hydrogen atoms were neglected in the analysis.