

difference, though significant, is, nevertheless, small, and does not correspond to more than a few calories per mole in the Pd-Cl bond energy.

The bond distances and angles of the norbornadiene molecule are compared with those reported for the free olefin obtained from an electron diffraction study by Schomaker (Wilcox, Winstein & McMillan, 1960) in Table 2. Some additional distances are given to indicate the degree of regularity in the structure. Since the reliability of the electron diffraction data is unknown, significant statements cannot be made about the agreement of the values. Using either the electron diffraction values or the values of 1.54 and 1.34 Å for single and double bonds as criteria of normalcy, it is evident that very little change in the olefin occurs on forming the complex. The double bonds which are coordinated are probably lengthened a small amount. The infrared spectrum, except for the uncertainty of

interpretation, appears to give a more sensitive indication of changes in the olefin.

References

- BAENZIGER, N. C., DOYLE, J. R. & CARPENTER, C. L. (1961). *Acta Cryst.* **14**, 303.
 BAENZIGER, N. C., DOYLE, J. R., RICHARDS, G. F. & CARPENTER, C. L. (1961). *Advances in the Chemistry of the Coordination Compounds*, pp. 131-138. New York: The Macmillan Co.
 CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 698.
 EVANS, H. T., JR. (1953). *Rev. Sci. Instrum.* **24**, 156.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 RICHARDS, G. F. (1964). Thesis.
 WILCOX, C. F., JR., WINSTEIN, S. & McMILLAN, W. G. (1960). *J. Amer. Chem. Soc.* **82**, 5450. The authors refer to unpublished data of V. Schomaker.

Acta Cryst. (1965). **18**, 926

Accuracy of an Automatic Diffractometer. Measurement of the Sodium Chloride Structure Factors

BY S. C. ABRAHAMS AND J. L. BERNSTEIN

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.

(Received 18 September 1964 and in revised form 13 October 1964)

The sodium chloride structure factors have been measured with the automatic diffractometer, PEXRAD. Five different single-crystal spheres were used, with various experimental measurement techniques. Analysis of the error in the measurements has shown the average structure factor (F_{meas}) for the best techniques to have a standard error of 3.5 to 4.0% $|F_{\text{meas}}|$. About half this error is due to instrumental causes. The remainder is produced by error in the absorption coefficients, crystal size determination, extinction coefficients *etc.* The mean values of the Debye-Waller factors are $B(\text{Na}) = 1.639 \pm 0.037$, $B(\text{Cl}) = 1.326 \pm 0.023 \text{ \AA}^2$, corresponding to a characteristic temperature $\theta = 287 \text{ }^\circ\text{K}$, in good agreement with the θ derived from specific heat and from elastic constant measurements. It is shown that low R values do not necessarily indicate the absence of systematic error.

Introduction

Automatic diffractometers are composed of two separate, intimately connected, systems. These are colloquially referred to as the *hardware* and *software* systems. By hardware is meant the assembly of mechanical, electronic and similar components; by software, the control and processing programs. A description of the hardware and software systems alone, while necessary for understanding the operation of an automatic diffractometer, is incomplete without a measure of the accuracy of the whole system. A subsidiary, although important, aspect of this total description includes the rate at which data are measured, and also the amount of personal time required in running the diffractometer.

In the case of one automatic diffractometer, PEXRAD*, both the hardware (Abrahams, 1962) and the software (Cetlin & Abrahams, 1963) systems have been described. In addition, an analysis has been made of the various sources of error common to all automatic diffractometer systems, and criteria have been presented (Abrahams, 1964a) for their detection. The present paper uses these criteria to assess the accuracy of PEXRAD under normal operating conditions. The best values obtained in this study for the Debye-Waller factors for the sodium and chlorine atoms in rocksalt are given. Typical times for measurement of structure factors, and the personal time involved in these measurements are also presented.

* Programmed Electronic X-ray Automatic Diffractometer.

Experimental conditions

A total of five spheres were ground, in a Bond (1951) type sphere grinder, using Harshaw Chemical Co. optical quality sodium chloride. The basic PEXRAD hardware (Abrahams, 1962) was used, together with the following equipment variables which will now be specified. Pulse height discrimination was used with all crystals, about 95% of the appropriate $K\alpha_1\alpha_2$ radiation (see Table 1) being transmitted. Both the focal source and the Supper Company standard Weissenberg collimator subtended about 1° at the crystal. The previously described detector was modified by optically coupling a thallium-activated sodium iodide crystal to an AmpereX 150-AVP-02 photomultiplier tube through a 7/32-inch thick Lustra glass light pipe. This assembly* forms a detector of great uniformity over the entire detection surface. The experimental conditions that varied from crystal to crystal are given in Table 1. In the case of crystals 1 and 2, a fixed counter aperture of 3° was used with β -filtered radiation.

Balanced filters, in a holder similar to that designed by McKinsty & Short (1960), were used for crystals 3, 4 and 5. For crystal 3, which was measured at an early stage of this study, the fixed 3° aperture was used. For crystals 4 and 5, the vertical aperture was operated automatically (Abrahams, 1963). The horizontal aperture was adjusted manually for each reciprocal layer. The apertures for crystals 4 and 5 were opened to the widths derived by Burbank (1962).

The software required, both to operate PEXRAD and produce structure factors from its punched paper tape output, has already been described (Cetlin & Abrahams, 1963). These programs were used without modification for crystals 1 and 2. For crystals 3, 4 and 5, several changes were made, of which the most important was handling the α - and balanced β -filtered radiation received by the counter. With PEXRAD, a complete reciprocal layer is first measured with the β and then remeasured with the α filter. The radiation received through the α filter at each location along the reciprocal lattice point profile is then subtracted from the corresponding β -filtered count. If either count exceeds the linearity range of the counting subsystem, an appropriate correction is made before the subtraction. The resulting profile, consisting of the counts measured at the number of locations indicated in Table 1, cor-

responds to that obtained with monochromatic radiation, broadened by the spectral distribution between the absorption edges of the α and β filters. The integrated intensity is now obtained from each such profile by numerical integration. The integration limits are experimentally determined, and correspond to the effective passband for the balanced filter pair.

The integrated intensity of every reflection was measured, for each crystal, within a hemisphere of reciprocal space for $(\sin \theta)/\lambda \leq 0.59 \text{ \AA}^{-1}$ for Cu $K\alpha$ and $(\sin \theta)/\lambda \leq 1.02 \text{ \AA}^{-1}$ for Mo $K\alpha$. Another program takes the structure factors, into which the integrated intensities have been converted, and collects all members of a given form. The mean value of each form then gives F_{meas} . The standard error in each F_{meas} is computed by the same program (see *Measurement of the NaCl structure factors* below). These mean structure factors are finally corrected for anomalous dispersion by Paterson's (1963) method.

Investigation of error varying systematically with θ

The estimation of error in the measured structure factor is comparable in importance to measurement of the structure factor itself. A discussion has already been given of many of the errors present in automatic diffractometer systems (Abrahams, 1964a). A largely objective method for estimating the total standard error in the measured structure factor has also been given (Abrahams, 1964b). Before this method is applied to the present series of measurements on sodium chloride, a further systematic source of error, *viz.* one dependent on scattering angle (θ), should first be considered. Error of this type is particularly hard to determine experimentally, except by use of more than one characteristic radiation. It can be detected by comparison of the ratios of a series of weak reflections, measured both with Mo $K\alpha$ and Cu $K\alpha$, since the structure factors have been corrected for anomalous dispersion. Table 2 contains the values of five such weak reflections, normalized to the lowest-angle structure factor in the group. Crystal 3, measured with Cu $K\alpha$ radiation, contains reflections in the range $27.0^\circ \leq \theta \leq 63.7^\circ$, as compared with Mo $K\alpha$ reflections measured from the same planes in crystal 5, for which $12.1^\circ \leq \theta \leq 24.4^\circ$.

In general, the structure factor ratios for crystal 3 agree with those for crystal 5 within 4%, or within 2% of the mean for both measurements. These differences, as discussed in the section on *Accuracy*, are not signi-

* Now manufactured as a unit by Harshaw Chemical Co.

Table 1. *Experimental conditions for each crystal*

| Crystal No. | Radius | Radiation | Filters | Counter aperture | Points per profile | Time per pt. | Rotation axis |
|-------------|------------------|--------------|---------|------------------|--------------------|--------------|-----------------|
| 1 | 0.125 ± 0.006 mm | Cu $K\alpha$ | Ni | Fixed | 91 | 10 sec* | [1 $\bar{1}$ 0] |
| 2 | 0.143 ± 0.005 | Cu $K\alpha$ | Ni | Fixed | 101 | 20 | [1 $\bar{1}$ 0] |
| 3 | 0.165 ± 0.005 | Cu $K\alpha$ | Ni/Y | Fixed | 161 | 5 | [100] |
| 4 | 0.163 ± 0.006 | Mo $K\alpha$ | Zr/Y | Variable | 91 | 5 | [100] |
| 5 | 0.225 ± 0.005 | Mo $K\alpha$ | Zr/Y | Variable | 91 | 5 | [1 $\bar{1}$ 0] |

* Except in *hhl*, for which 50-sec counts were made.

Table 2. Structure factor ratios as a function of wavelength

| hkl | $F_{\text{meas}}/F(311)$ | | $F_{\text{meas}}/F(311)$ | |
|-----|--------------------------|------------------------------|--------------------------|------------------------------|
| | Crystal 3 | $\theta(\text{Cu } K\alpha)$ | Crystal 5 | $\theta(\text{Mo } K\alpha)$ |
| 311 | 1.00 | 27.0° | 1.00 | 12.1° |
| 331 | 0.89 | 36.6 | 0.92 | 15.9 |
| 333 | 0.87 | 45.3 | 0.88 | 19.1 |
| 351 | 0.94 | 54.0 | 0.91 | 21.9 |
| 335 | 0.84 | 63.7 | 0.81 | 24.4 |

ficant. PEXRAD may hence be regarded as free from significant error that is systematic with scattering angle.

Measurement of the NaCl structure factors

The values of the averaged structure factors measured for crystals 1 and 2 have already been given (Abrahams, 1964a). The mean values for crystal 3 are given in Table 3, for crystal 4 in Table 4 and for crystal 5 in Table 5. Tables 3, 4 and 5 also contain the values for the estimated standard errors in F_{meas} under σF_{meas} . These values are calculated by the program referred to under *Experimental conditions*, in which $\sigma F_{\text{meas}} = [\sigma^2(\bar{F}^2_{\text{meas}})]^{1/2}/2\bar{F}_{\text{meas}}$, where

$$\sigma^2(\bar{F}^2_{\text{meas}}) = V(\bar{F}^2) + \bar{\sigma}^2(\bar{F}^2) + c\bar{F}^4 \quad (\text{Abrahams, 1964b}),$$

$$\bar{F}^2_{\text{meas}} = \frac{1}{R} \sum_{j=1}^R F_{j\text{meas}}^2,$$

$$V(\bar{F}^2) = \frac{1}{R-1} \sum_{j=1}^R (F_{j\text{meas}}^2 - \bar{F}^2_{\text{meas}})^2$$

and $\bar{\sigma}^2(\bar{F}^2) =$

$$\left[\frac{\Delta\varphi}{t} \right]^2 \left\{ \sum_{n+1}^{k-n} N_j + \left(\frac{k}{2n} - 1 \right)^2 \left[\sum_1^n N_j + \sum_{k-n+1}^k N_j \right] \right\} [A \cdot \text{Lp}]^{-2},$$

with $\Delta\varphi$ the angular interval through which the crystal is rotated between counts, t the time taken per count, k the number of points used in the profile and n the number of background points on each side of the peak. For crystal 3, $c=0.0027$; for crystal 4, $c=0.0020$ and for crystal 5, $c=0.0016$.

Thermal parameters

The magnitudes of F_{meas} and σF_{meas} in Tables 3, 4 and 5 were used in separate least-squares refinements of the scale factor, $B(\text{Na})$, and $B(\text{Cl})$ for each crystal. The atomic scattering factors were taken from *International Tables* (1962) for these calculations. The Bus-ing, Levy & Martin (1962) ORFLS program modified by B. B. Cetlin was used, resulting in the values given

Table 3. Measured† and calculated structure factors for NaCl crystal 3

| hkl | F_{meas} | σF_{meas} | F_{calc} | hkl | F_{meas} | σF_{meas} | F_{calc} | hkl | F_{meas} | σF_{meas} | F_{calc} |
|-----|-------------------|--------------------------|-------------------|-----|-------------------|--------------------------|-------------------|-----|-------------------|--------------------------|-------------------|
| 111 | 19.07 | 0.60 | 19.64 | 331 | 9.12 | 0.57 | 9.11 | 531 | 9.58 | 0.63 | 9.25 |
| 200 | 84.42 | 2.32 | 82.61 | 420 | 43.38 | 2.20 | 42.03 | 442 | 27.49 | 2.33 | 28.01 |
| 220 | 64.20 | 4.86 | 65.73 | 224 | 36.41 | 2.52 | 37.73 | 600 | 29.98 | 1.12 | 28.01 |
| 113 | 10.24 | 0.73 | 9.80 | 115 | 10.17 | 0.39 | 9.34 | 620 | 26.33 | 1.74 | 25.59 |
| 222 | 50.43 | 1.99 | 55.08 | 333 | 8.87 | 0.28 | 9.34 | 335 | 8.65 | 0.67 | 8.86 |
| 400 | 51.50 | 2.09 | 47.63 | 440 | 32.48 | 1.19 | 30.70 | 226 | 21.80 | 0.74 | 23.38 |

† These F_{meas} have been corrected for secondary extinction, using Zachariasen's (1963) method, with the experimental constant $C = 0.049 \times 10^{-6}$.

Table 4. Measured and calculated structure factors for NaCl crystal 4

| hkl | F_{meas} | σF_{meas} | F_{calc} | hkl | F_{meas} | σF_{meas} | F_{calc} | hkl | F_{meas} | σF_{meas} | F_{calc} |
|-----|-------------------|--------------------------|-------------------|-----|-------------------|--------------------------|-------------------|--------|-------------------|--------------------------|-------------------|
| 111 | 17.55 | 0.49 | 19.62 | 551 | 8.34 | 0.30 | 8.49 | 448 | 9.74 | 0.30 | 9.78 |
| 200 | 66.25† | 4.93 | 83.24 | 640 | 22.01 | 0.68 | 21.66 | 771 | 4.41 | 0.22 | 4.51 |
| 220 | 62.08 | 2.54 | 66.74 | 642 | 19.86 | 0.67 | 20.05 | 339 | 4.31 | 0.24 | 4.51 |
| 113 | 10.23 | 0.34 | 9.67 | 731 | 7.81 | 0.26 | 7.83 | 557 | 4.44 | 0.18 | 4.51 |
| 222 | 57.17 | 1.54 | 56.36 | 553 | 7.56 | 0.24 | 7.83 | 10,0,0 | 8.99 | 0.26 | 9.14 |
| 400 | 51.53 | 1.43 | 49.11 | 800 | 17.54 | 0.51 | 17.22 | 860 | 8.81 | 0.37 | 9.14 |
| 331 | 9.52 | 0.29 | 9.00 | 337 | 6.77 | 0.32 | 7.11 | 10,2,0 | 8.60 | 0.40 | 8.54 |
| 420 | 44.82 | 1.58 | 43.66 | 446 | 15.82 | 0.57 | 16.02 | 862 | 8.45 | 0.45 | 8.54 |
| 224 | 38.72 | 1.04 | 39.47 | 820 | 16.17 | 0.46 | 16.02 | 773 | 3.81 | 0.23 | 4.00 |
| 333 | 9.75 | 0.26 | 9.32 | 660 | 14.87 | 0.72 | 14.90 | 951 | 4.07 | 0.11 | 4.00 |
| 115 | 9.72 | 0.30 | 9.32 | 228 | 15.28 | 0.42 | 14.90 | 666 | 7.68 | 0.29 | 8.00 |
| 440 | 32.38 | 0.90 | 32.57 | 751 | 6.25 | 0.34 | 6.38 | 2,2,10 | 8.19 | 0.26 | 8.00 |
| 531 | 9.38 | 0.34 | 9.34 | 555 | 6.45 | 0.20 | 6.38 | 953 | 3.39 | 0.27 | 3.53 |
| 442 | 29.71 | 0.82 | 29.93 | 662 | 13.54 | 0.64 | 13.85 | 864 | 6.84 | 0.31 | 7.02 |
| 600 | 30.51 | 1.17 | 29.93 | 840 | 13.25 | 0.40 | 12.88 | 10,4,0 | 6.92 | 0.27 | 7.02 |
| 620 | 27.49 | 0.76 | 27.52 | 119 | 5.71 | 0.22 | 5.72 | 10,4,2 | 6.75 | 0.18 | 6.57 |
| 335 | 8.87 | 0.28 | 9.05 | 753 | 5.48 | 0.22 | 5.72 | 880 | 5.53 | 0.35 | 5.77 |
| 226 | 25.00 | 1.05 | 25.32 | 842 | 12.53 | 0.33 | 12.01 | 882 | 5.46 | 0.37 | 5.43 |
| 444 | 23.21 | 0.65 | 23.38 | 664 | 10.96 | 0.44 | 11.22 | 4,4,10 | 5.39 | 0.26 | 5.43 |
| 117 | 8.70 | 0.23 | 8.49 | 931 | 5.17 | 0.26 | 5.08 | | | | |

† Omitted from the least squares refinement - see "Discussion."

Table 5. Measured and calculated structure factors for NaCl crystal 5

| <i>hkl</i> | F_{meas} | σF_{meas} | F_{calc} | <i>hkl</i> | F_{meas} | σF_{meas} | F_{calc} | <i>hkl</i> | F_{meas} | σF_{meas} | F_{calc} |
|------------|--------------------|--------------------------|-------------------|------------|-------------------|--------------------------|-------------------|------------|-------------------|--------------------------|-------------------|
| 111 | 18.77 | 0.53 | 19.62 | 551 | 8.20 | 0.39 | 8.39 | 448 | 9.46 | 0.42 | 9.27 |
| 200 | 73.06 [†] | 2.25 | 83.04 | 640 | 21.47 | 0.61 | 20.01 | 771 | 4.36 | 0.62 | 4.37 |
| 220 | 63.21 | 1.92 | 66.41 | 642 | 19.70 | 0.74 | 19.41 | 339 | 4.36 | 0.36 | 4.37 |
| 113 | 10.40 | 0.35 | 9.70 | 731 | 7.53 | 0.33 | 7.71 | 557 | 3.99 | 0.33 | 4.37 |
| 222 | 54.31 | 1.62 | 55.94 | 553 | 7.41 | 0.47 | 7.71 | 10,0,0 | 8.06 | 0.66 | 8.63 |
| 400 | 48.71 | 1.50 | 48.63 | 800 | 16.45 | 0.50 | 16.60 | 860 | 8.73 | 0.35 | 8.63 |
| 331 | 9.59 | 0.29 | 9.02 | 337 | 6.69 | 0.36 | 6.97 | 10,2,0 | 8.12 | 0.44 | 8.05 |
| 420 | 43.70 | 1.23 | 43.12 | 446 | 15.51 | 0.54 | 15.40 | 862 | 8.16 | 0.46 | 3.05 |
| 224 | 38.75 | 1.25 | 38.90 | 820 | 15.62 | 0.62 | 15.40 | 773 | 3.74 | 0.35 | 3.86 |
| 333 | 9.17 | 0.91 | 9.31 | 660 | 14.42 | 0.72 | 14.29 | 951 | 3.91 | 0.38 | 3.86 |
| 115 | 9.62 | 0.30 | 9.31 | 228 | 14.58 | 0.55 | 14.29 | 666 | 7.07 | 0.33 | 7.52 |
| 440 | 32.54 | 0.98 | 31.95 | 751 | 6.10 | 0.41 | 6.24 | 2,2,10 | 7.70 | 0.32 | 7.52 |
| 531 | 9.47 | 0.30 | 9.29 | 555 | 5.97 | 0.37 | 6.24 | 953 | 3.84 | 0.28 | 3.39 |
| 442 | 29.28 | 1.01 | 29.29 | 662 | 13.20 | 0.61 | 13.26 | 864 | 6.71 | 0.39 | 6.57 |
| 600 | 29.49 | 0.84 | 29.29 | 840 | 12.42 | 0.56 | 12.31 | 10,4,0 | 6.61 | 0.42 | 6.57 |
| 620 | 27.18 | 0.99 | 26.88 | 119 | 5.22 | 0.45 | 5.57 | 10,4,2 | 6.16 | 0.44 | 6.14 |
| 335 | 8.47 | 0.53 | 8.97 | 753 | 5.35 | 0.42 | 5.57 | 880 | 5.28 | 0.39 | 5.37 |
| 226 | 24.68 | 1.02 | 24.68 | 842 | 12.03 | 0.59 | 11.45 | 882 | 4.91 | 0.50 | 5.04 |
| 444 | 22.19 | 0.87 | 22.74 | 664 | 10.24 | 0.81 | 10.67 | 4,4,10 | 4.99 | 0.25 | 5.04 |
| 117 | 8.18 | 0.32 | 8.39 | 931 | 4.85 | 0.54 | 4.93 | | | | |

[†]Omitted from the least squares refinement - see "Discussion."

in Table 6. The parameters obtained with crystals 4 and 5 are regarded as more reliable than those measured with crystal 3, primarily owing to use of Mo $K\alpha$ rather than Cu $K\alpha$ radiation. In addition to the smaller absorption corrections and increased number of data, correct counter apertures were used rather than the fixed aperture used with crystal 3 which masks the edges of the higher angle reflections. The standard deviations in Table 6 partially reflect the relative reliability of the measurements.

Table 6. Sodium chloride temperature factors

| | Crystal 3 | Crystal 4 | Crystal 5 |
|----------------------------------|-------------|---------------|---------------|
| Scale factor | 1.04 ± 0.03 | 0.995 ± 0.009 | 1.036 ± 0.008 |
| $B(\text{Na})$ (Å ²) | 1.91 ± 0.16 | 1.588 ± 0.023 | 1.689 ± 0.024 |
| $B(\text{Cl})$ (Å ²) | 1.48 ± 0.13 | 1.295 ± 0.017 | 1.357 ± 0.017 |
| Number of observations | 18 | 58 | 58 |
| R | 0.044 | 0.026 | 0.022 |

The values obtained with crystals 4 and 5 will hence be used as the best measures of the sodium chloride thermal parameters. Although these values are not expected to be significantly different from each other, examination of the $B(\text{Na})$ and $B(\text{Cl})$ magnitudes for crystals 4 and 5 shows an apparent statistical difference. Use of the Student t -distribution, where $t = (x_1 - x_2) / (\sigma^2 x_1 + \sigma^2 x_2)^{1/2}$, indicates that an event has occurred whose probability is only 0.003, under the assumption that the two $B(\text{Na})$ values are the same. For $B(\text{Cl})$, the corresponding probability is 0.012. Both probabilities are small, and in the absence of further information it would be necessary to conclude that the results from the two crystals are different. The following analyses demonstrate this conclusion to be incorrect.

The F_{meas} values in both Tables 4 and 5 were used (omitting $F(200)$ from both sets) in a joint least-squares refinement of S_4 , S_5 (the scale factors for crystal 4 and crystal 5), $B(\text{Na})$ and $B(\text{Cl})$. The resulting values are $S_4 = 1.007 \pm 0.007$, $S_5 = 1.021 \pm 0.007$, $B(\text{Na}) = 1.628 \pm 0.017$ and $B(\text{Cl}) = 1.321 \pm 0.012$, with $R = 0.024$ and $wR = 0.034$. The distribution of $(F_{\text{meas}} - F_{\text{calc}}) / \sigma F_{\text{meas}}$, for each of the 58 observations on crystal 4, versus the corresponding quantity for crystal 5, yielded an equivalent normal deviate of +2.0. The two independent sets of F_{meas} hence have a strong positive correlation, showing them both to belong to the same population. An anomalous situation thus arises, since there is an apparently significant difference between the least-squares results for S , $B(\text{Na})$ and $B(\text{Cl})$ obtained from the two data sets separately, and the conclusion from the joint analysis that the two sets are not systematically different.

A complementary method for analyzing these results is due to Hamilton (1965), who uses significance tests on the ratios of weighted R factors to decide whether individual R factors are improved or impaired by given changes in the observations or the model. If it is assumed that the two measured sets of data belong to the same normal population, and also that the observational equations in the least-squares model are linear, then the ratio of weighted R factors obtained between F_{meas} for crystal 4 and F_{calc} for crystal 5 to that given for crystal 4 in Table 8 should be less than 1.13 at the 0.005 significance level. This ratio is found to be 1.225. Similarly for the wR factor ratio obtained between F_{meas} for crystal 5 with the F_{calc} for crystal 4 to that given for crystal 5 in Table 8: this also should be less than 1.13, at the 0.005 significance level, as compared with 1.270 found. One, or more, hypothesis is thus indicated to be incorrect. It

is most interesting, however, to consider the F_{calc} values obtained from the joint analysis with the two F_{meas} sets. In this case, the wR factor ratio for crystal 4 becomes 1.031 and for crystal 5 it is 1.071, *i.e.* the two independent sets of F_{meas} do not differ (at the 0.005 significance level), with respect to the parameters obtained in the joint analysis.

Another and independent indication that the thermal parameters derived from the F_{meas} in Tables 4 and 5 are probably not significantly different is as follows. An unintentional programming mistake resulted in the error term $0.0016\bar{F}^4$ (see *Accuracy*) for crystal 5 being replaced by $0.0016\bar{F}^2$, thus essentially eliminating this constant. All values of σF_{meas} were hence too small, by a factor of about two on average. Least-squares refinement, using weights given by the incorrect σF_{meas} , gave $B(\text{Na}) = 1.746 \pm 0.024$, $B(\text{Cl}) = 1.367 \pm 0.018 \text{ \AA}^2$, with $R = 0.025$. This value of $B(\text{Na})$ differs from that in Table 6 by 0.057 \AA^2 , more than half the difference between the values for $B(\text{Na})$ from crystals 4 and 5 in Table 6, showing the uncertainty in B to be greater than the calculated standard error.

It is concluded that there is probably no real difference between the thermal parameters obtained from crystals 4 and 5, but instead the individual standard errors derived from the least-squares refinement are probably too small. The average of these values is hence better than the individual values, resulting in $B(\text{Na}) = 1.639 \text{ \AA}^2$, $B(\text{Cl}) = 1.326 \text{ \AA}^2$.

An alternative measure of the error in the average Debye-Waller factors can be estimated from the expression

$$\{[(1.639 - 1.588)^2 + (1.639 - 1.689)^2]/2(2 - 1)\}^{\pm} = 0.050 \text{ \AA}^2$$

for $B(\text{Na})$ and

$$\{[(1.326 - 1.295)^2 + (1.326 - 1.357)^2]/2(2 - 1)\}^{\pm} = 0.031 \text{ \AA}^2$$

for $B(\text{Cl})$. This unbiased estimate of error can be combined with that obtained from the joint least-squares calculation, of 0.017 \AA^2 for $B(\text{Na})$ and 0.012 \AA^2 for $B(\text{Cl})$, by averaging the two independent estimates of variance for each Debye-Waller factor. The resulting estimate for the standard error is then 0.037 \AA^2 for $B(\text{Na})$ and 0.023 \AA^2 for $B(\text{Cl})$.

Accuracy

An objective estimate of the standard error in each mean structure factor is given under σ_{meas} in Tables 3, 4 and 5. These individual estimates may be averaged using the relation:

$$R(\text{expected}) = \frac{\sum_{j=1}^n \sigma F_{j\text{meas}}}{\sum_{j=1}^n F_{j\text{meas}}}$$

Table 7 contains the values of R (expected) together with the traditional, and analogous, R (observed) for comparison. For the case of crystals 4 and 5, the average error in F_{meas} is hence about 3.5–4.0%. This error contains two distinct parts (Abrahams, 1964*b*), cor-

responding to an instrumental and an experimental but non-instrumental error. In both crystals 4 and 5, the latter (absorption, crystal size, *etc.*) is about 2–2.5%. It may be noted that the expectation value for $||F_{\text{meas}} - F_{\text{calc}}||$ is not necessarily equal to σF_{meas} , but is a function of the distribution.

Table 7. *Expected and observed R-factors*

| | Crystal 3 | Crystal 4 | Crystal 5 |
|----------------|-----------|-----------|-----------|
| R (expected) | 0.049 | 0.035 | 0.039 |
| R (observed) | 0.044 | 0.026 | 0.022 |

A similar, and more valid, comparison can be made between the expected and observed *weighted R* factors, since it is the sum of the weighted squared differences between measured and calculated structure factors that is minimized by the least-squares refinement. Table 8 contains these weighted R factors, which also indicate the average structure factor to have an error of about 3–4%. It should be observed that the variation in error magnitude for any individual structure factor is likely

Table 8. *Expected and observed weighted R factors*

| | Crystal 3 | Crystal 4 | Crystal 5 |
|-----------------|-----------|-----------|-----------|
| wR (expected) | 0.042 | 0.034 | 0.041 |
| wR (observed) | 0.055 | 0.033 | 0.032 |

to form a normal distribution. Increasing the time per count, and hence the number of counts in each reflection, only decreases the percentage error in $\sigma^2(\bar{F}^2)$ as defined above if $\bar{\sigma}^2(\bar{F}^2)$ is larger than or comparable to $V(\bar{F}^2) + cF^4$. For most NaCl reflections, this condition is not met, *e.g.* based on the relative scale of the measurements for crystal 4,

$$\bar{F}(733) = 111.7, \quad \bar{\sigma}^2 F^2(733) = 0.429 \times 10^3 \text{ and}$$

$$V[\bar{F}^2(733)] + 0.0020\bar{F}^4(733) = 1.469 \times 10^6.$$

Measurement time

The rate at which measurements, necessary for obtaining integrated intensities, are made is clearly a function of both the time spent collecting counts at each position along the profile through the reciprocal lattice points, and of the number of positions defining each profile. Table 1 contains this information for each crystal measured. The rate is, further, a function of set-up time between reflections and also elapsed time between successive counts. Table 9 gives the number of reflections measured in a 24 hour period together with the total number measured (including all redundancies) for each crystal. It should be noted that for crystals 3, 4 and 5, balanced filters were used, resulting in each measurement being made twice. The *effective* number of reflections measured each day is hence half that given in Table 9 for these three crystals.

The IBM 7094 computing time required to process the PEXRAD output paper tape through the various stages to give a final set of averaged measured structure

Table 9. *Measurement times for the NaCl crystals*

| Crystal No. | Number of reflections measured in 24 hours | Total number of reflections | Computing time per reflection |
|-------------|--|-----------------------------|-------------------------------|
| 1 | 84 | 186 | 0.044 sec |
| 2 | 40 | 186 | 0.044 |
| 3 | 86 | 179 | 0.095 |
| 4 | 160 | 780 | 0.076 |
| 5 | 160 | 780 | 0.076 |

factors (but excluding use of the dispersion correction or least-squares refinement programs) is also given in Table 9. Once the crystal is correctly set up, and assuming PEXRAD is operating normally, the amount of personal time required on PEXRAD is, typically, about 15 minutes per reciprocal lattice level. In addition, a further 10 minutes per day is usually required for renewing the supply of output paper tape (in routine operation 2000 feet is commonly consumed in about 24 hours) and for making a variety of standard checks.

Discussion

It has been demonstrated, for the measurements made on sodium chloride crystals 4 and 5, that the average error (σF_{meas}) in the average structure factor (F_{meas}) is given approximately by $\sigma F_{\text{meas}} = 0.035 - 0.040 |F_{\text{meas}}|$, of which slightly more than half is due to instrumental causes. This average error estimate includes the error due to thermal diffuse scattering (TDS) at the nominal level of $0.01 |F_{\text{meas}}|$. Nilsson (1957) has shown that the TDS component received by the counter can be considerably larger than this. An indirect test of the presence of TDS in the present work is made by determination of the characteristic temperature θ from the expression

$$M = \frac{6h^2T}{mk\theta^2} \left[\Phi(x) + \frac{x}{4} \right] \frac{\sin^2 \theta}{\lambda^2} \quad (\text{James, 1948}),$$

where M is the average Debye-Waller factor for sodium chloride, obtained from the individual B values and weighted linearly by the atomic masses. In the present investigation, $M = 1.449 (\sin^2 \theta)/\lambda^2$. The corresponding value of θ is then 287 °K. This may be compared with Renninger's (1952) value of 319 °K, which was reduced to 302 °K by Nilsson after correction for the TDS. The characteristic temperature derived from specific heat measurements is 281 °K, and from the elastic constants is 303 °K.

A TDS correction in the present case, which could be comparable with that made by Nilsson, would reduce our value to about 260 °K. In the absence of a rigorous calculation for the effect of TDS on the present measurements, the error in this low θ value, which is acceptable relative to the specific heat and elastic constant characteristic temperatures, is unknown. For the purposes of this paper, the experimental magnitudes of B and M , uncorrected for thermal diffuse scattering, may be regarded as our final values. Table 10 contains these values together with some recent com-

Table 10. *Comparison of the Debye-Waller factors for NaCl at 296 °K*

| $B(\text{Na})$ | $B(\text{Cl})$ | M | Reference |
|---------------------------------|---------------------------------|-----------------------|--------------------------------|
| $1.639 \pm 0.037 \text{ \AA}^2$ | $1.326 \pm 0.023 \text{ \AA}^2$ | 1.449 \AA^2 | Present work |
| 1.63 ± 0.04 | 1.42 ± 0.01 | 1.50 | Levy, Agron & Busing (1963) |
| 1.615 | 1.575 | 1.590 | Buyers & Smith (1963) |
| — | — | 1.475 | Barron, Berg & Morrison (1957) |

parable sets. It is apparent that the present values are in fair agreement with those obtained by neutron diffraction (Levy, Agron & Busing, 1963). Both sets, however, are liable to error caused by TDS present under the Bragg peaks. The approximate correction for TDS in the X-ray value of M is about $+0.1$ to 0.2 , which brings it into excellent agreement with the recent theoretical work of Buyers & Smith (based on the normal mode data of Karo & Hardy). The thermal data of Barron, Berg & Morrison (1957) however yields an M value lying closely between the TDS uncorrected X-ray and neutron values.

Extinction is another source of error which should be discussed. In the least-squares calculation based on the values of F_{meas} in Tables 4 and 5, the strong low order reflection $F(200)$ was omitted. This is the only term that appears to be extinction-reduced by an amount greater than the estimated error in the term. The presence of appreciable extinction raises the possibility that crystals 4 and 5 might possess different extinction coefficients because of differences in texture. The Debye-Waller factors for these two crystals, in such a case, could then appear to be slightly different, in accord with the experimental findings. That grinding a small sphere out of a pure sodium chloride single crystal does not necessarily produce an ideally imperfect crystal is demonstrated by the extinction present in crystal 3. Similar observations on the varying degrees of imperfection in rocksalt have been made by previous workers.

Finally, some observations should be made about the significance of low R factors. In crystals 1 and 2 (Abrahams, 1964a) the R factors were 0.021 and 0.038 (also 0.044 for a repeated measurement set on crystal 2). Within the standard errors obtained by the least-squares method, the Debye-Waller values for crystal 1 are in agreement with the present best set (Table 10). The B values from crystal 2, for both sets, are however very significantly different. For crystal 3, with $R = 0.026$, the B values are in agreement. The values of F_{meas} obtained in a careful powder diffractometer study of sodium chloride by Vihonen (1960) were entered in a least-squares refinement, using the same program and scattering factors as for the present data, to determine the corresponding Debye-Waller factors. These were found to be:

$$B(\text{Na}) = 1.327 \pm 0.017, \quad B(\text{Cl}) = 1.128 \pm 0.010 \text{ \AA}^2,$$

with $R=0.014$. These B values are very significantly different from those in Table 10. These results suggest that identification of low R factors with the absence of systematic error can be highly misleading.

It is a pleasure to thank Miss B. B. Cetlin for assistance with all the PEXRAD programs, Dr R. D. Burbank for valuable discussions on intensity measurement and Dr W. C. Hamilton and Dr C. L. Mallows for penetrating comment and suggestions on statistical matters.

References

- ABRAHAMS, S. C. (1962). *Rev. Sci. Instrum.* **33**, 973.
 ABRAHAMS, S. C. (1963). *Rev. Sci. Instrum.* **34**, 1279.
 ABRAHAMS, S. C. (1964a). *Acta Cryst.* **17**, 1190.
 ABRAHAMS, S. C. (1964b). *Acta Cryst.* **17**, 1327.
 BARRON, T. H. K., BERG, W. T. & MORRISON, J. A. (1957). *Proc. Roy. Soc. A* **242**, 478.
 BOND, W. L. (1951). *Rev. Sci. Instrum.* **22**, 344.
 BURBANK, R. D. (1962). Unpublished work. See also *Acta Cryst.* **17**, 434 (1964).
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). Oak Ridge National Lab. Rept. TM-305.
 BUYERS, W. J. L. & SMITH, T. (1963). Private communication. See also *Acta Cryst.* **16**, A90 (1963).
 CETLIN, B. B. & ABRAHAMS, S. C. (1963). *Acta Cryst.* **16**, 943.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
International Tables for X-Ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 JAMES, R. W. (1948). *Optical Principles of the Diffraction of X-Rays*. London: Bell and Sons.
 LEVY, H. A., AGRON, P. A. & BUSING, W. R. (1963). Amer. Cryst. Assoc. Meeting, Cambridge, Mass., Paper E-7.
 MCKINSTRY, A. A. & SHORT, M. A. (1960). *J. Sci. Instrum.* **37**, 178.
 NILSSON, N. (1957). *Ark. Fysik*, **12**, 247.
 PATTERSON, A. L. (1963). *Acta Cryst.* **16**, 1255.
 RENNINGER, M. (1952). *Acta Cryst.* **5**, 711.
 VIHENEN, S. (1960). *Suom. Tied. Toim. Ann. Acad. Scient. Fenn.* A VI. **52**, 7.
 ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1965). **18**, 932

The Crystal and Molecular Structure of 7,7,8,8-Tetracyanoquinodimethane*

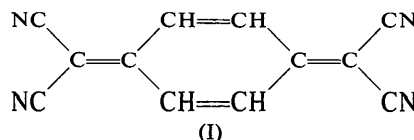
BY ROBERT E. LONG, ROBERT A. SPARKS† AND KENNETH N. TRUEBLOOD

Department of Chemistry‡, University of California, Los Angeles, California 90024, U.S.A.

(Received 24 July 1964)

TCNQ forms orange-red monoclinic crystals belonging to space group $C2/c$, with $a_0 = 8.906$, $b_0 = 7.060$, $c_0 = 16.395$ Å, $\beta = 98.54^\circ$, and four centrosymmetric molecules in the unit cell. The structure was solved by conventional Patterson methods and independently by a computer search of possible structures consistent with reasonable molecular packing. It was refined by full-matrix least-squares methods. The molecule, which has essentially mmm symmetry, librates through a r.m.s. amplitude of about 5.5° about its long axis. The bond distances are in good accord with the predictions of simple molecular orbital theory.

Tetracyanoquinodimethane (I) (TCNQ) is one of a series of novel cyano-olefins prepared in recent years (Cairns *et al.*, 1958; Acker & Hertler, 1962), and is of especial interest not only because it forms unusually stable molecular complexes containing the radical anions $TCNQ^-$ and $(TCNQ)_2^-$, but also because some of these crystalline complexes are semi-conductors and show other unusual solid-state properties (Melby, Harder, Hertler, Mahler, Benson & Mochel, 1962).



The present study of the detailed molecular geometry and packing of TCNQ in the pure crystalline state was undertaken partly because of the intrinsic interest of the molecule itself and partly to provide a standard for comparison for proposed studies of some of the complexes containing the aforementioned radical anions.

Experimental

Orange-red chunky crystals of TCNQ which had been purified by sublimation were supplied to us by R. E.

* This work was supported by the Directorate of Chemical Sciences of the U.S. Air Force Office of Scientific Research, Grant AF-AFOSR-240-63.

† Present address: Computing Center, University of Hawaii, Honolulu 14, Hawaii.

‡ Contribution No. 1720.