at small angles in curve A, use of the correction terms C_k will eliminate most of the error.

The unsmearing process was tested in practice by applying it to some experimental scattering curves obtained in a study of aluminum hydroxide gel (Bale, 1959). The results indicate that the unsmearing process can be used routinely in analysis of scattering data. For the curves considered, the accuracy of the data did not justify calculation of the C_k.

Equation (4) is in a form which allows relatively easy programming for a digital computer. As the T_{kj} are the same for all experimental curves using the same equipment, a point on the unsmeared curves can be calculated in a few minutes with a desk computer when tables of the T_{kj} are available. The authors can supply tables of the T_{kj} and C_k for $\Delta h = 0{\cdot}001$ rad. and

$$p = \tfrac{1}{8}225(\pi)^{\frac{1}{2}}.$$

Although a smooth curve may often be used instead of the actual data points in numerical calculation from (3) or (4), there is nothing in the collimation correction method that requires the use of a smooth curve. There may be occasions when it is preferable to use the actual data points in (3) or (4).

Fig. 2 shows the effect of the unsmearing process on a curve containing a series of maxima. The scattering curve calculated for infinitely high collimating slits and spherical particles (Schmidt, 1955) was used for the experimental curve. The unsmearing procedure sharpens the maxima of the experimental curve, and the unsmeared curve agrees well with the spherical scattering curve for perfect collimation.

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Temperature Variation of the Lattice Constant and the Coefficient of Thermal Expansion of Sodium Chlorate

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Using a back-reflection, flat-film camera and an extrapolation technique, precision determination of the lattice constant of sodium chlorate has been made at different temperatures between the range 30–232 °C. From these, by a graphical treatment, the coefficients of thermal expansion at various temperatures have been evaluated. An equation is also given for evaluating the coefficient of expansion at any temperature.

These coefficients of expansion show a temperature rate of variation higher than the one reported by Sharma (1950*a*) from macroscopic measurements. An explanation for this difference is attempted in terms of imperfections in a single crystal.

Introduction

Sodium chlorate has been the subject of numerous studies because of its simple structure and many of its interesting properties. Zachariasen (1929) gave the length of the unit cell as 6·570 ± 0·006 kX. (6·583 Å). Hüber (1940) studied the mixed crystals of sodium chlorate and sodium bromate and gave the lattice constant of sodium chlorate as 6·568* ± 0·001 Å. Solheim, Konrad & Vegard (1947) report a value of 6·5722* (converted from kX. to Å units). In view of the discrepancies in these values an accurate redetermination of the lattice constant was thought to be worthwhile.

Data on the thermal expansion of this salt have been reported by Mason (1946) and Sharma (1950*a*). Mason quotes the mean values obtained by Miss Armstrong

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* These values are taken from *Structure Reports*.

over the range of temperature 0–90 °C. Sharma has covered a wider range of temperature from 25–230 °C., using an interferometric method. No X-ray determination of the coefficient of thermal expansion has so far been reported. It was felt that such an investigation might prove interesting by way of comparison with the results obtained by the optical method. The present paper reports a systematic precision determination of the lattice constant of sodium chlorate at various temperatures between 30 °C. and 232 °C. The coefficient of thermal expansion at various temperatures has been evaluated and its temperature variation over this range has been studied.

Experimental

1. *Lattice constant at room temperature.* Room temperature value of the size of the unit cell was obtained with the help of a 11·46 cm. cylindrical powder camera. The procedure followed was the same as has already been described in an earlier communication (Deshpande, Sirdeshmukh & Mudholker, 1959).

2. *Lattice constant at elevated temperatures.* A Seifert back-reflection, flat-film camera was used to obtain pictures at different temperatures. The specimen-holder and heater were of such a design that the specimen could be heated to and maintained at any desired temperature and the temperature could be measured with a calibrated copper-constantan thermocouple to an accuracy of ± 1 °C. The constancy of the temperature over the duration of the exposure was ensured by using constant-voltage d.c. for heating.

3. *Evaluation of the films.* The films recorded seven well-resolved $\alpha_1\alpha_2$ doublets at room temperature with Cu $K\alpha$ radiation, the one at the highest angle being the reflection with $N(=h^2+k^2+l^2)=72$. At elevated temperatures, reflections $N=73$ and $N=74$ were also recorded.

An observation made repeatedly may be mentioned here. It was observed that above 200 °C. the lines showed some splitting. Although small in magnitude, the splitting was quite appreciable for the line with $N=74$. The exact significance of this observation is under further investigation. However, we have used the centre of gravity of the intense component of these lines for ring-diameter measurements.

Table 1. *X-ray data for* $NaClO_3$

Line No.	Radiation Cu K	N = $(h^2+k^2+l^2)$	$\sin^2\theta$	$\cos\varphi-\cos^2\varphi$	a (Å)
1	α_1	65	0·89252	0·169	6·5733
2	α_2	65	0·89662	0·164	6·5745
3	α_1	66	0·90589	0·153	6·5746
4	α_2	66	0·91050	0·147	6·5742
5	α_1	68	0·93326	0·116	6·5749
6	α_2	68	0·93778	0·109	6·5753
7	α_1	69	0·94684	0·095	6·5754
8	α_2	69	0·95158	0·087	6·5753
9	α_1	70	0·96040	0·073	6·5759
10	α_2	70	0·96519	0·065	6·5759
11	α_1	72	0·98755	0·024	6·5769
12	α_2	72	0·99234	0·015	6·5773

Film No. (20). Radiation: Cu $K\alpha_1=1·54050$ Å.
$T=32$ °C. Cu $K\alpha_2=1·54434$ Å.
Film-to-specimen distance = 7·1 cm.
Specimen: Recrystallized sodium chlorate powder of controlled particle size.

The films were measured on a Philip's comparator with an accuracy of 0·005 cm. Random errors were minimised by repeated and independent measurements.

Table 2. *Comparison of the values of 'a' obtained by different cameras*

Camera	Film No.	T (°C.)	a_T (Å)	a_{15} (Å)	Mean
Philips (A)	16	36·5	6·5787	6·5729	6·5727
Philips (B)	21	36	6·5785	6·5725	
Seifert back-reflection	19	31	6·5770	6·5724	6·5725
	20	32	6·5774	6·5726	

It is a well-known fact that the Bragg angles of the various reflections calculated from the films suffer from certain systematic errors. These errors have been studied and appropriate corrections for this type of camera have also been evaluated (Peiser, Rooksby & Wilson, 1955). Hess (1951) has shown that the errors in the diffraction angle $\varphi(=\pi-2\theta)$ due to film shrinkage and inaccurate film-to-specimen distance are proportional to $\sin\varphi\cos\varphi$. One of the authors (Deshpande, 1955) has examined in detail all possible systematic errors inherent in the geometry of the camera used. These include double coating of the films, absorption of X-rays and oblique incidence, besides the two considered by Hess. It is shown that the total error in the ring diameters is approximately proportional to $\sin\varphi\cos\varphi$, which in turn leads to a fractional error in the lattice constant proportional to $\cos\varphi-\cos^2\varphi$. Therefore, if the lattice constants obtained from individual reflections are plotted against this function, a linear extrapolation is possible. (See also Cullity, 1956). Using this extrapolation technique the films gave consistent values of the lattice constant at the corresponding temperature, an example being given in Table 1 and Fig. 1. The best straight line was fitted by the method of least squares. Table 2 gives a comparison between the values of a obtained by

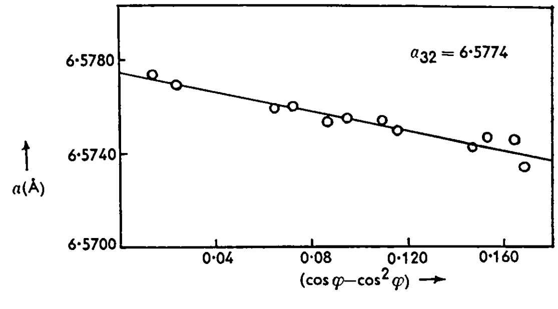

Fig. 1. Plot of a against $(\cos\varphi-\cos^2\varphi)$.

this method and those obtained from a full picture taken with a cylindrical camera. The agreement is quite satisfactory.

a_T was reduced to a_{15}, for the sake of comparison with earlier reports, with the coefficient of expansion given by Mason ($43·4\times10^{-6}$ °C.$^{-1}$).

Mean value of a at 15 °C. from the two types of cameras:

$$a_{15} = 6·5726 \pm 0·0002 \text{ Å} .$$

Lattice constant at elevated temperatures

Table 3 gives the values of the lattice constant obtained at different temperatures and its temperature variation is shown in Fig. 2.

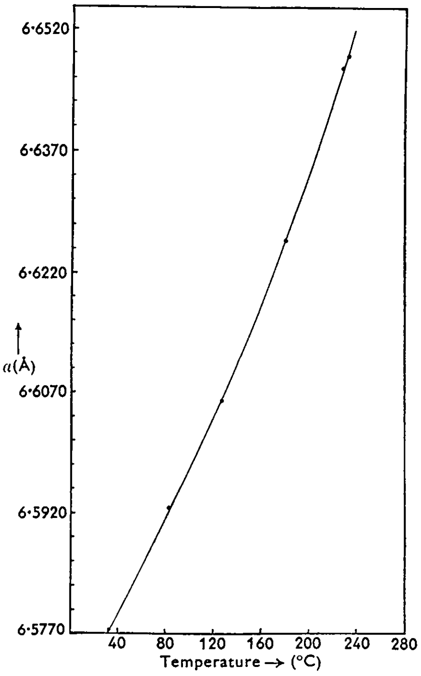

Fig. 2. Plot of lattice constant against temperature.

Table 3. *Lattice constant of* $NaClO_3$ *at various temperatures*

Film No.	T (°C.)	a (Å)
19	31	6·5770
20	32	6·5774
63	82·5	6·5926
69	127·5	6·6060
86	180	6·6261
87	227	6·6475
89	232	6·6491

Thermal expansion

From a carefully drawn graph of temperature and lattice constant, values of a were read at regular intervals of 20 °C. From these, the coefficients of expansion at the mean temperature of the interval were derived using the definition $\alpha_{20} = (1/a_{20})(\Delta a/\Delta T)$. The results are given in Table 4. This graphical treatment introduces some uncertainties in the evaluation of $\Delta a/\Delta T$ and it follows that the values of the coefficient of expansion given in column 2 of Table 4, will reflect these errors. However, if a graph is drawn between these values and temperature, a smooth curve (Fig. 3) could be drawn through these points and the authors feel that this curve smooths out the uncertainties mentioned above and represents the correct temperature variation of α.

Table 4. *Coefficient of expansion of* $NaClO_3$ *at various temperatures*

T (°C.)	α from the definition	α from equation (1)	$\Delta\alpha$ (%)	α from Sharma's eq.
40	$41·83\times10^{-6}$	$41·82\times10^{-6}$	...	$45·30\times10^{-6}$
50	43·35	42·51	+2·0	45·96
60	44·87	43·32	+3·5	46·63
70	45·63	44·23	+3·1	47·32
80	45·63	45·27	+0·8	48·03
90	47·16	46·43	+1·5	48·75
100	48·68	47·71	+2·0	49·48
110	50·20	49·10	+2·2	50·23
120	50·20	50·62	−1·8	51·00
130	51·72	52·26	−1·0	51·77
140	53·24	54·01	−1·4	52·56
150	54·00	55·89	−3·3	53·37
160	57·80	57·88	...	54·19
170	60·85	59·99	+1·4	55·02
180	62·37	62·23	+0·2	55·87
190	62·37	64·57	−3·4	56·74
200	65·41	67·05	−2·4	57·62
210	71·49	69·63	+2·6	58·51
220	73·78	72·34	+1·9	59·42

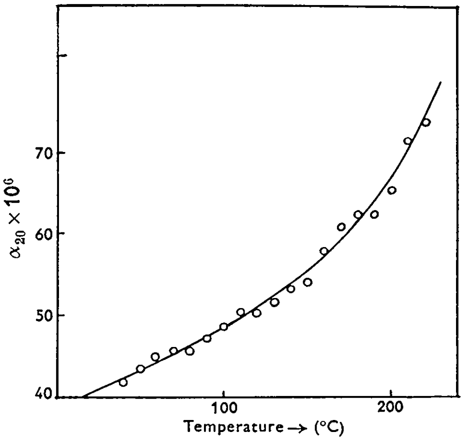

Fig. 3. Plot of α_{20} against temperature.

By a least-squares treatment of the data given in the first and second column of Table 4, the following equation was obtained for the curve giving the temperature variation of the coefficient of expansion over the range of temperature used.

$$\alpha_T = 4·029\times10^{-5} + 1·459\times10^{-8}T + 5·959\times10^{-10}T^2. \quad (1)$$

Discussion

1. *Lattice constant at room temperature.* Although it was not possible for us to ascertain the temperature at which Solheim, Konrad & Vegard (1947) have made their measurements, our value of the lattice constant at 15 °C., as given in Table 2, is in good agreement with the one they have reported. We have also calculated the density of the substance at 15 °C. using the value of the Avogadro number as suggested by Straumanis (1949). The calculated density, 2·489 g.cm.$^{-3}$, is also in good agreement with the experimentally determined value, 2·49 g.cm.$^{-3}$ (I.C.T.).

2. *Thermal expansion.* In column 3 of Table 4 are given the values of α_T calculated from equation (1). Column 4 gives the percentage differences between these values and those in column 2. The maximum difference is 3·5%. In view of the fact that the values in column 2 were derived from a graphical treatment of the data, the agreement may be said to be satisfactory. The authors feel that equation (1) is accurate to within 3%. However, above 200 °C., because of the line splitting observed the error may be greater. The values of α_T as calculated from Sharma's equation (1950*a*) are entered in column 5.

A comparative study of the coefficients of expansion at different temperatures given by Sharma and the present work shows that Sharma's values near room temperature are slightly higher by about 5% than those reported here; this is roughly within the combined limits of errors. The present work gives a higher gradient for the α–T curve, so that at higher temperatures the X-ray values are much larger than the macroscopic values. The melting point of sodium chlorate is 248 °C. and it is possible that the coefficient of expansion will increase rapidly as the melting point is approached.

Although it is not possible to give any exact reason for this discrepancy, a plausible explanation could be given in terms of crystal imperfections. It is an established fact that, in general, single crystals have a mosaic structure in which small blocks with perfect lattice structure are packed together with small amounts of misorientation. It is also known from X-ray intensity measurements that polishing of crystal faces disrupts the regular crystal structure. The degree of this imperfection depends to some extent on the nature of the crystal and also on the history of mechanical treatment. Sharma (1950*b*) and Eucken & Dannohl (1934), both using macroscopic methods, have reported values of the coefficients of expansion of lithium fluoride at various temperatures. Their results show a marked difference in the gradients of the α–T curves. This disagreement may be attributed to the mosaic imperfections of varying degree in the two specimens. Gott (1942) has also suggested that the existence of Schottky type of defects, which increase with increasing temperature, will give smaller X-ray values than the corresponding macroscopic values. Gott's conclusions have been supported by Colby & Connell (1948) but not by Connell & Martin (1951). In view of the above observations, we wish to present the following qualitative picture.

In a single crystal at ordinary temperature both mosaic and Schottky defects are present in varying degrees. When the temperature is increased there are two consequences: firstly, each mosaic block will show a small expansion due to increase in Schottky defects in addition to the usual lattice expansion; secondly, these mosaic blocks will try to readjust themselves in the crystal and the misorientation will decrease. The second factor will conceal, to some extent, the true lattice expansion in macroscopic investigations. The adjustment of the mosaic blocks will progressively increase with rising temperature and will be more or less complete near the melting point. Thus the net macroscopic expansion will be made of three components as shown in the following relation:

$$\alpha_{\text{macroscopic}} = \alpha_{\text{lattice}} + \alpha_{\text{Schottky}} - \alpha_{\text{readjustment}}\,.$$

Depending upon the relative values of the last two components on the right hand side, the X-ray values of the coefficients of expansion will be smaller or greater than the macroscopic values. At sufficiently high temperatures, the readjustments will be taking place at a high rate and hence the X-ray values of the coefficients of expansion will be larger than the macroscopic values.

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