We may calculate the estimated standard deviations from the method of least squares as applied to

$$\phi=\sum_{3}\frac{1}{f_r}(|F_o|-|F_c|)^2$$

in the manner of B (§3). Using C (3·7) and assuming $A_{hk}$, etc., small compared with $A_{hh}$, we have, corresponding to B (3·7) for the estimated standard deviation $\sigma(x_r)$ of the $x$ co-ordinate of the $r$th atom in a non-centrosymmetric structure,

$$\sigma^2(x_r)=-2\sigma^2/(VA_{hh}), \quad (1)$$

where $\sigma$ is the estimated standard deviation of an observation of unit weight.

For a structure having only a centre of symmetry we find, corresponding to C (3·7),

$$c_{mn}=\sum_{3}4\pi^2\frac{hk}{ab}f_r\{2\sin(\theta_r-\alpha)\}^2$$

$$=-2VA_{hk},$$

so that $$\sigma^2(x_r)=-\sigma^2/(2VA_{hh}). \quad (2)$$

On comparing (1) and (2) we see that, for the same $\sigma$ and $A_{hh}$, the estimated co-ordinate standard deviations of non-centrosymmetric structures are twice those of centrosymmetric structures.

This result may also be reached via the Fourier method, for by using C (§3·1) we see that the total error is twice that estimated by assuming errors in the $|F|$'s but none in the phase angles, which is the assumption made for centrosymmetric structures.

The mistake in the argument given previously in A occurs between equations A (11·20) and A (11·21). It was stated that the $\Delta\alpha$ occurring in the contribution of the finite-series correction error was identical with that in A (11·20). This is incorrect, the $\Delta\alpha$ of the finite-series correction error should be the difference between the phase angles of the 'calculated' structure and a 'true' structure based on the 'calculated' positions.

A mistake also occurs in equation A (11·8); the sign of $\sin(-\theta_1)$ is incorrectly given as positive.

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## Increase in *Q*-value and reduction of aging of quartz crystal blanks.

By A. C. Prichard, M. A. A. Druesne and D. G. McCaa, *Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey, U.S.A.*

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The importance of quartz crystal units for frequency control derives from the very high $Q$ (ratio of reactance to resistance) and the low frequency–temperature coefficient of quartz, and the very steep slope of the reactance curve of the crystal blank. The $Q$ of quartz is higher than that of any other frequency-controlling device used to date.

The $Q$ and frequency of a given quartz crystal blank change, however, with time; these changes are results of the so-called aging process. During World War II, crystal units were used in very large quantities in military communications equipment. Considerable difficulty was experienced during the first years of the war because the useful life of a crystal unit was greatly reduced by reason of its 'aging out of frequency' or 'going dead'. A usable reduction in aging was later accomplished during 1944 by etching the surfaces of the crystal blanks. This only mitigated the effect, however, and its more complete elimination was highly desirable.

A method has recently been developed at the Signal Corps Engineering Laboratories, Fort Monmouth, N.J., whereby the $Q$-value of the quartz blank has been materially increased, and the aging has been very greatly reduced. The method consists of annealing the quartz blank by heating it almost to the inversion temperature of quartz, or 500° C., and cooling it down extremely slowly.

This simple treatment yields values of $Q$ which are at least double those of untreated quartz blanks, and variations in frequency and $Q$ are minute. These improvements in $Q$ and aging characteristics appear to be of a permanent character.

A paper describing the results in greater detail is in preparation.

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## Observations on the diffuse X-ray reflexion of sodium chlorate, $NaClO_3$.

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### Introduction

In the course of a systematic study of the elastic properties of cubic substances by means of diffusely reflected X-rays the authors have had occasion to study crystals of sodium chlorate. Garrido (1948) has published an account of photographic observations of X-rays diffusely reflected from this substance and we were surprised to find that our results differed considerably from his. It is, of course, possible to calculate the form of the isodiffusion surface around any reciprocal-lattice point. This only involves the elastic constants and has been worked out by Sen (1949). This calculation gives a result not in agreement with Garrido's observations. In this note we wish to put on record a direct experimental test of the variation of the intensity of diffuse reflexion round two reciprocal points, namely, 600 and 333.

## Experimental method

A full description of the apparatus used in this research will appear elsewhere but it may be briefly described as follows. The source of X-rays was a G.E.C. CA-6 copper tube and the characteristic radiation was reflected from a bent quartz crystal. (For monochromator see Wooster, Ramachandran & Lang (1949).) After passing through the collimating slits the X-ray beam passed through a small ionization chamber without windows. The ionization current produced in the air was measured and used to standardize the intensity of the incident X-rays. The rays fell upon an extended surface of the crystal and were reflected into a Geiger–Müller tube. The pulses of the Geiger-Müller tube were amplified and recorded in the way described by Wooster *et al.* (1948). Two crystals grown from aqueous solution were used, one having a natural (100) face and the other a ground and etched (111) plane. The crystal and Geiger–Müller tube were set so as to explore a section of the isodiffusion surface surrounding each of the reciprocal-lattice points 600 and 333. To trace out this section a large number of points were determined and the mean line was then drawn through them. The setting of the crystal and Geiger–Müller tube was greatly facilitated by use of charts giving in reciprocal space, on the scale of 50 cm. $=\lambda^{-1}$, the loci of points corresponding respectively to constant angles of incidence and scattering.

## Results

The results of the observations on the isodiffusion surfaces for 600 and 333 are given in Figs. 1 and 2. These diagrams are plotted on an arbitrary scale in reciprocal space. In each figure the experimentally determined points for the isodiffusion surface corresponding to 40 counts per minute lie between the two full lines, the distance between which corresponds to the possible statistical error. For any one observation this error is about ± 3 %. The dots represent points on the isodiffusion surface calculated from the elastic constants, $c_{11}=4\cdot 90$, $c_{12}=1\cdot 39$, $c_{44}=1\cdot 17\times 10^{11}$ dyne cm.$^{-2}$ (Mason, 1946), using the formula given by Jahn (1942), namely,

$$I\propto r^{-2}\{c_{44}^2+\Sigma L^2[c_{44}(c_{11}-c_{44})(m^2+n^2) + (c_{11}+c_{12})(c_{11}-c_{12}-2c_{44})m^2n^2] - 2\Sigma MNmn(c_{12}+c_{44})[c_{44}+(c_{11}-c_{12}-2c_{44})l^2]\}$$
$$\div\{c_{11}c_{44}^2+c_{44}(c_{11}+c_{12})(c_{11}-c_{12}-2c_{44})(m^2n^2+n^2l^2+l^2m^2) + (c_{11}+2c_{12}+c_{44})(c_{11}-c_{12}-2c_{44})^2 l^2m^2n^2\},$$

where $I$ = intensity of diffuse reflexion at a (small) distance $r$,

$r$ = radius vector of isodiffusion surface,

$L=h/\sqrt{(h^2+k^2+l^2)}$, etc., where $(hkl)$ are the indices of the reciprocal point at the centre of the isodiffusion surface,

and $l$, $m$, $n$ = direction cosines of $r$.

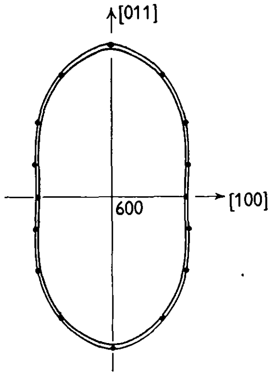

Fig. 1.

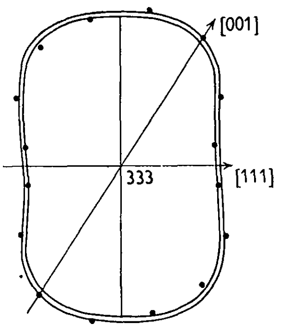

Fig. 2.

Fig. 1. Experimentally determined isodiffusion surface (full lines) and calculated position of isodiffusion surface (dots) for 600 reciprocal point of $NaClO_3$.

Fig. 2. Experimentally determined isodiffusion surface (full lines) and calculated position of isodiffusion surface (dots) for 333 reciprocal point of $NaClO_3$.

It will be seen that the agreement between the experimental observations and the theoretical points on the isodiffusion surface is satisfactory. Complete agreement is not to be expected since corrections for the second-order diffuse reflexion and for the vertical divergence of the X-ray beam have not been made. These corrections would be small and as they require special study for their determination they were neglected in this work. Additional support for the applicability of the above formula was found in the study of the section of the isodiffusion surface around the reciprocal point 600 by a plane normal to the axis [100] and passing through the point 600. Experimentally this section was found to be circular; theoretically it should also be circular and of radius proportional to $1/c_{44}$. Garrido's figure on the other hand shows an isodiffusion surface of the form shown in Fig. 3, which accords neither with our experimental observations nor with the computed surface. A section of the isodiffusion surface passing through 200 and normal to the axis [010] was also determined. This was similar to Fig. 1 and the calculated isodiffusion surface agreed with the experimental one. In this particular section, Garrido's isodiffusion surface is qualitatively similar to what is calculated from the elastic constants, but no proper comparison can be made as his work was not expressed quantitatively.

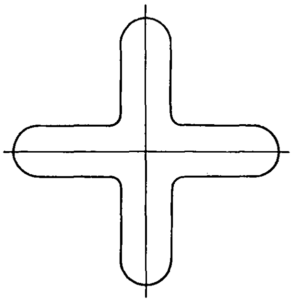

Fig. 3. Diagrammatic sketch showing isodiffusion surface for 200 reciprocal point of $NaClO_3$ in the plane 100, according to Garrido (1948). (The corresponding surface about the reciprocal point 600 is theoretically of the same form as that about the point 200.)

Thus, there is disagreement between Garrido's observations and those described here on the isodiffusion surfaces of sodium chlorate. It may be mentioned that the crystals used in this study were chosen because of their perfection as judged by the eye and also by the narrowness of the Bragg reflexion peak.

One of us (W. A. W.) wishes to acknowledge gratefully a grant from the D.S.I.R. for assistance in this work; one of us (G. N. R.) thanks the Commissioners of the 1851 Exhibition for a scholarship which made possible a period of research in England.

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## Hysteresis ranges of polymorphic transitions of some crystals.

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The polymorphic transitions which many substances undergo upon change of temperature are of considerable theoretical interest in the study of crystal chemistry and have been used experimentally to provide fixed points for temperature calibration (Buerger, Buerger & Chesley, 1943). The transition usually involves a change in the vibrational or rotational energy state of one of the ionic or molecular constituents, and generally occurs at an appreciably lower temperature when the high-temperature form is cooled than when the low-temperature form is heated. The separation of these two temperatures may be called a hysteresis range for the transition; its extent is found to vary widely among different crystals. Superheating or supercooling is to be expected in most transitions. It is also expected that the transitions will be somewhat sensitive to changes in pressure.

In an attempt to obtain a number of transition temperatures which might be used as 'fixed' points for calibration by the Buerger method of an electrically heated furnace for an X-ray powder camera, a survey of the literature was made. Considerable disagreement as to the value of each transition temperature was found, and information concerning the hysteresis range was meager. In order to correlate and evaluate these data it was necessary to study each transition experimentally. Measurements were made using reagent-grade samples placed inside carefully insulated containers which could be immersed in a constant-temperature oil bath or placed inside a controlled-temperature oven so as to provide slow, uniform heating or cooling toward a fixed temperature about 30° C. beyond the transition range. Temperatures of the samples were measured with fine-wire thermocouples calibrated against standardized Anschutz thermometers and read by means of a potentiometer circuit at intervals of $\frac{1}{2}$ min. or 1 min. Plateaus or inflections in the heating- or cooling-rate curves gave the transition temperatures.

Transition ranges have been studied carefully for potassium perchlorate, cesium perchlorate, and for two of the four known transitions of ammonium nitrate. It was found that the transitions for increasing temperature occurred at the same temperature ($t_H$) on each successive trial for a particular compound, but that the amount of superheating varied with the heating rate and with the history of the sample. Similarly, the transition toward the lower-energy form occurred at a sensibly constant temperature ($t_C$) on successive trials following a variable amount of supercooling. In cases of extreme superheating or supercooling the amount of energy involved in some transitions may be insufficient to return the sample to the transition point. The values of $t_H$ and $t_C$ determined for the substances named are given in Table 1.

The amounts of superheating and supercooling observed were small (less than 1° C.) except for the orthorhombic–

Table 1. *Results of this investigation*

| Substance | Transition | $t_H$ (° C.) | $t_C$ (° C.) | Hysteresis ($t_H-t_C$) (° C.) |
|---|---|---|---|---|
| $NH_4NO_3$ | orth.–tet. | 84·4 | 83·7 | 0·7 |
| | tet.–cubic | 125·6 | 125·3 | 0·3 |
| $CsClO_4$ | orth.–cubic | 218·6 | 203·8 | 14·8 |
| $KClO_4$ | orth.–cubic | 299·6 | 294·0 | 5·6 |

Table 2. *Results of other investigators*

| Investigator | $KClO_4$ (° C.) | $CsClO_4$ (° C.) | $NH_4NO_3$ tet.–cubic (° C.) | $NH_4NO_3$ orth.–tet. (° C.) |
|---|---|---|---|---|
| Buerger *et al.* (1943) | 295·7 | — | 126·2 | 85·4 |
| Early & Lowry (1919) | — | — | 125·2 | 84·2 |
| Zawidsky (1904) | — | — | 125·0 | 85·4 |
| Herman & Ilge (1930) | 299·5 | 219 | — | — |
| Vorlander & Kaascht (1923): | | | | |
| (Heating) | 299·5 | 219–221 | — | — |
| (Cooling) | 293·0 | 197–204 | — | — |
| *International Critical Tables* (1927) | 300 ± < 5 | 219 ± > 5 | 125·3 ± 0·2 | 83·9 ± < 1 |