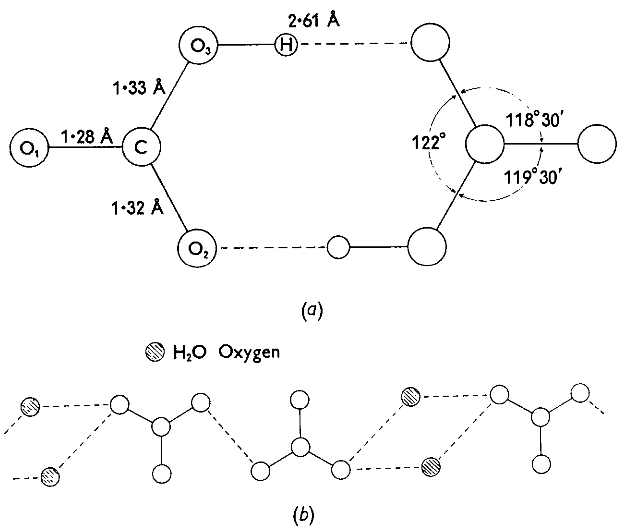

Fig. 5. (*a*) Schematic diagram of the bicarbonate ion in the potassium salt. (*b*) Schematic diagram of the hydrogen bond system in sodium sesquicarbonate.

in the dimeric vapor (Karle & Brockway, 1944) and 1·24 and 1·29 Å in the solid (Jones & Templeton, 1958).

It is tempting to draw comparisons between the dimeric forms of these acids in the vapor state and the dimeric bicarbonate ions in the potassium salt, and similarly between the infinite chain systems of these acids in the solid state with the corresponding bicarbonate chains in the sodium salt. A more valid comparison would result however if data were available for the crystal structures of other carboxylic acids such as propanoic, butyric, valeric, etc. Work on these acids has been started and will be discussed in future papers.

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Thermal Expansion of Triglycine Sulphate

By S. Ganesan

Department of Physics, Indian Institute of Science, Bangalore 12, *India*

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The thermal expansion of triglycine sulphate, which exhibits ferroelectric behaviour, has been investigated both below and above the Curie point by the interferometric method. Along all the directions studied there is an abrupt reversal of sign of the expansion coefficient at the Curie point. Investigations carried out with various rates of heating and cooling have shown that there is no thermal hysteresis. The shortest hydrogen bond in the unit cell of the crystal is found to coincide with the direction of maximum expansion. The results are compared with the X-ray measurements of Ezhkova *et al.* (1959).

Introduction

Triglycine sulphate $(NH_2CH_2COOH)_3H_2SO_4$ crystallizes in the monoclinic system and is found to be ferroelectric at room temperature (Matthias *et al.*, 1956). Morphological and X-ray studies of Matthias *et al.* (1956) and Hoshino *et al.* (1957) have shown that the space group is $P2_1$ in the ferroelectric phase, and above the Curie point of 47 °C. the space group is $P2_1/m$. The crystal belongs to the uniaxial ferroelectric group and the direction of spontaneous polarization is the diad *b*-axis of the crystal. Later workers have given the Curie point to be about 50 °C. (Triebwasser, 1958; Fatuzzo, 1958).

Hoshino *et al.* (1957), Triebwasser (1958) and Fatuzzo (1958) reported a pronounced anomaly of the dielectric constant at the Curie point, but obeying Curie–Weiss law above the Curie point. The Curie–Weiss temperature obtained by them agrees with the transition temperature. The temperature dependence of the spontaneous polarization is also found to be a continuous function of temperature. These studies evidently indicate that the transition in triglycine sulphate is of the second order.

The specific heat has been measured through the transition point by Hoshino *et al.* (1957) from 0 to 80 °C. The specific-heat curve exhibits a hump at the transition temperature of 47 °C. from which they have concluded that this is a typical case of a second-order transition which is not of the usual λ type. The structure of the crystal has been determined in the polar phase by Hoshino *et al.* (1959). The structure of the polar-phase is slightly distorted from that of the non-polar phase, in that the mirror symmetry present above the Curie point is removed below the Curie point. The whole structure is maintained by hydrogen bonds. The short hydrogen bond of length 2·438 Å between glycine II and glycinium III is believed to be responsible for the switching mechanism. In a closely linked crystal the 'flipping' of the hydrogen produces changes in other parts, leading to a reversal of polarization. The axial system chosen by Hoshino *et al.* (1959) is followed in the present work.

One of the important uses of the thermal expansion studies is the analysis of phase transitions. Since the thermal expansion coefficient is the second-order derivative of the Gibbs free energy it will show a discontinuity for a second-order phase transition. Hence an investigation of the thermal expansion of triglycine sulphate would give us information about the nature of phase transition. The thermal expansion of single crystals of triglycine sulphate and its temperature variation have been investigated in detail both below and above the transition temperature. A preliminary report of the results obtained was communicated to *Nature* (Ganesan, 1960). Fuller details are published here.

Experimental

Single crystals of triglycine sulphate were grown by the method of slow evaporation from aqueous solution of a mixture of glycine and sulphuric acid, in stoichiometric molar ratio. Transparent flawless crystals of size 2·5 cm. square and thickness 1 cm. with well-developed faces were obtained. The thermal expansion of this crystal has been studied with the interferometric technique in use in this laboratory (Press, 1949; Sridhar, 1952).

Since the crystal is monoclinic, four measurements, one along the diad axis b and the other three in the (010) plane, had to be made for determining the principal expansion coefficients and to fix the orientation of the expansion ellipsoid. The directions chosen were the b-axis, a-axis, c-axis and a direction perpendicular to the a-axis. Observations were carried out on the specimens, while they were heated slowly through the transition temperature.

Results

Along the b-axis the crystal first contracts on heating up to the transition point. At the transition point there is an abrupt reversal of the sign of the expansion coefficient and the crystal then expands. This reversal of sign in the expansion coefficient is clearly seen since the fringes start moving in the opposite direction after the transition point. The contraction or expansion is tested by pressing a rod slightly on the top quartz plate of the interferometer without disturbing the arrangement and observing the direction of motion of the fringes.

The measurements were carried out along the b-axis from −75 to about 100 °C. through the transition temperature. From −75 °C. to the transition point, the crystal is found to contract. The magnitude of the negative expansion coefficient in this direction decreases gradually from −75 to 0 °C. and starts increasing thereafter. The contraction becomes greater as the transition point is reached.

Along the c-axis the same range of temperature was covered. The crystal expands first up to the transition temperature, the magnitude of the expansion coefficient increasing until the transition point is reached. After the transition point, the crystal contracts but the contraction is small.

Along the a-axis below room temperature the crystal does not show any expansion or contraction. Above room temperature up to the transition point the specimen expands but the magnitude of the expansion coefficient is small. Above the transition temperature it contracts.

In the fourth direction, i.e. perpendicular to the a-axis, the behaviour is similar to that along c-axis. The crystal expands up to the transition point and then contracts.

Table 1. *Expansion coefficients*

Temp.	Along a-axis $\alpha_a \times 10^6$	Along b-axis $\alpha_b \times 10^6$	Along c-axis $\alpha_c \times 10^6$	Along normal to a-axis $\alpha_{\perp a} \times 10^6$
−40 °C.	Nil	−21·0	38·0	26·0
−20	Nil	−15·5	52·0	40·0
20	1·5	−8·0	84·0	82·0
40	14·0	−23·0	128·0	134·0
60	−39·0	57·5	−8·0	−12·0
80	−44·0	61·5	−14·0	−18·0

The coefficients of expansion in different directions and their temperature variations are given in Table 1 and exhibited in Figs. 1(a) and 1(b). A possible explanation for the contraction along b-axis below the transition point may be given. The very large expansion along c-axis below the Curie point can cause a Poisson contraction along the b-axis which might outweigh the normal expansion in that direction. A similar explanation may hold for the contraction along the c and a axes above the transition temperature since the crystal expands along b-axis now.

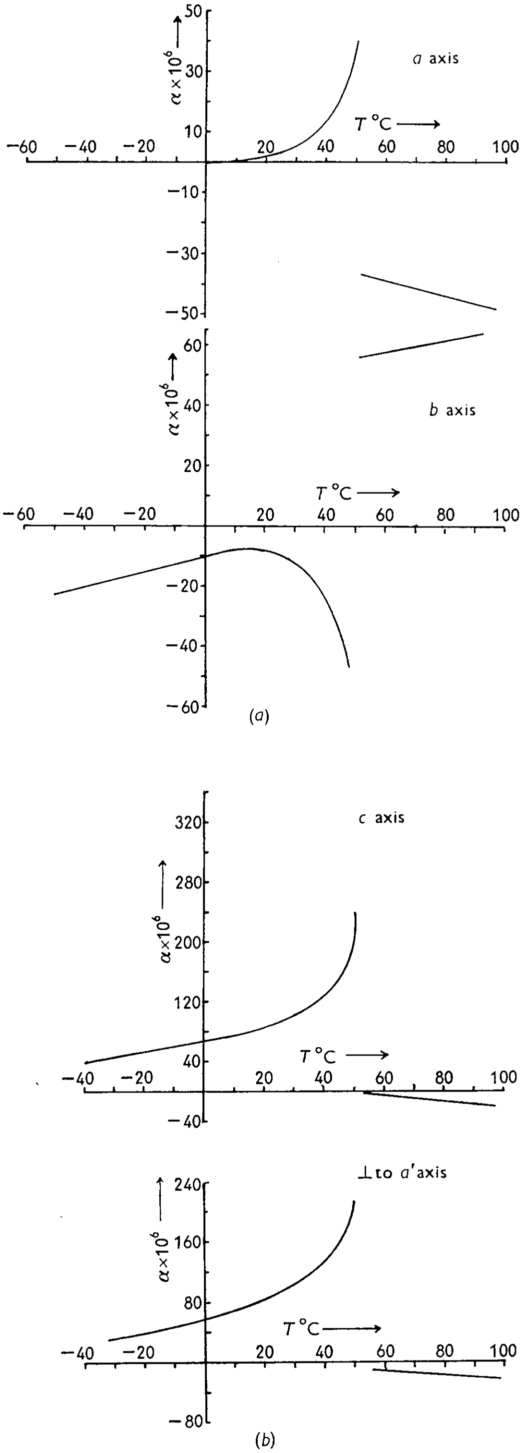


Fig. 1. (a) The linear thermal expansion coefficient versus temperature in triglycine sulphate along a-axis and b-axis. (b) The linear thermal expansion coefficient versus temperature in triglycine sulphate along c-axis and perpendicular to the a-axis.

Though the direction of movement of the fringes is reversed at the transition point the fringe transit is continuous with temperature. This shows that the changes in linear dimensions of the crystal take place continuously through the transition point indicating that the transition is of second order. This is in agreement with the results of dielectric studies in this crystal.

From the curves of α versus T it is clearly seen that the thermal expansion coefficient exhibits a sudden jump at the transition point in all the four directions examined. This sudden discontinuity is of the λ type which is in line with the usual anomalies associated with second-order transitions.

It was observed that while heating the crystal at about 0·6 °C./min. the transition point as deduced by the reversal in the direction of the fringe movement occurred around 51–52 °C. which is higher than the Curie point determined by dielectric studies. The transit of the fringes was observed while cooling and the transition occurred around 46 °C.; it thus appeared that there was a large thermal hysteresis (Ganesan, 1960). A similar large hysteresis was observed by Husimi & Kataoka (1959) in the piezoelectric coefficient d_{23} when the crystals were heated and cooled. While heating, the piezoelectric constant reaches a maximum value at 50 °C., but on cooling the maximum is attained around 47 °C. Recently Zarembovitch (1960) has reported some measurements on the ultrasonic velocity in this crystal using the diffraction of light by ultrasonic waves. In this case a sudden jump in the velocity occurs at 50 °C. while heating and at 47 °C. while cooling. This aspect of thermal hysteresis has been examined in some detail below.

For a second-order transition simple thermodynamic theory predicts that there should be no thermal hysteresis. Triebwasser (1958) states very definitely that there is no thermal hysteresis in the dielectric properties while heating and cooling the specimens. But before any definite statement can be made, it is obviously necessary to carry out the investigations at varying rates of heating to find out whether the difference in transition temperatures is preserved in the limit of zero rate of heating. It is quite possible for a sluggish transition to simulate hysteresis when it is heated rapidly. All the three directions a, b and c were chosen for study and the expansion coefficient was determined over a complete cycle while heating and cooling the specimens. Every specimen was taken through the transition point a few times so that the hysteresis cycle settles down to a permanent shape. The experiments were carried out for three different rates of heating and cooling, 25 μv/min., 15 μv/min.

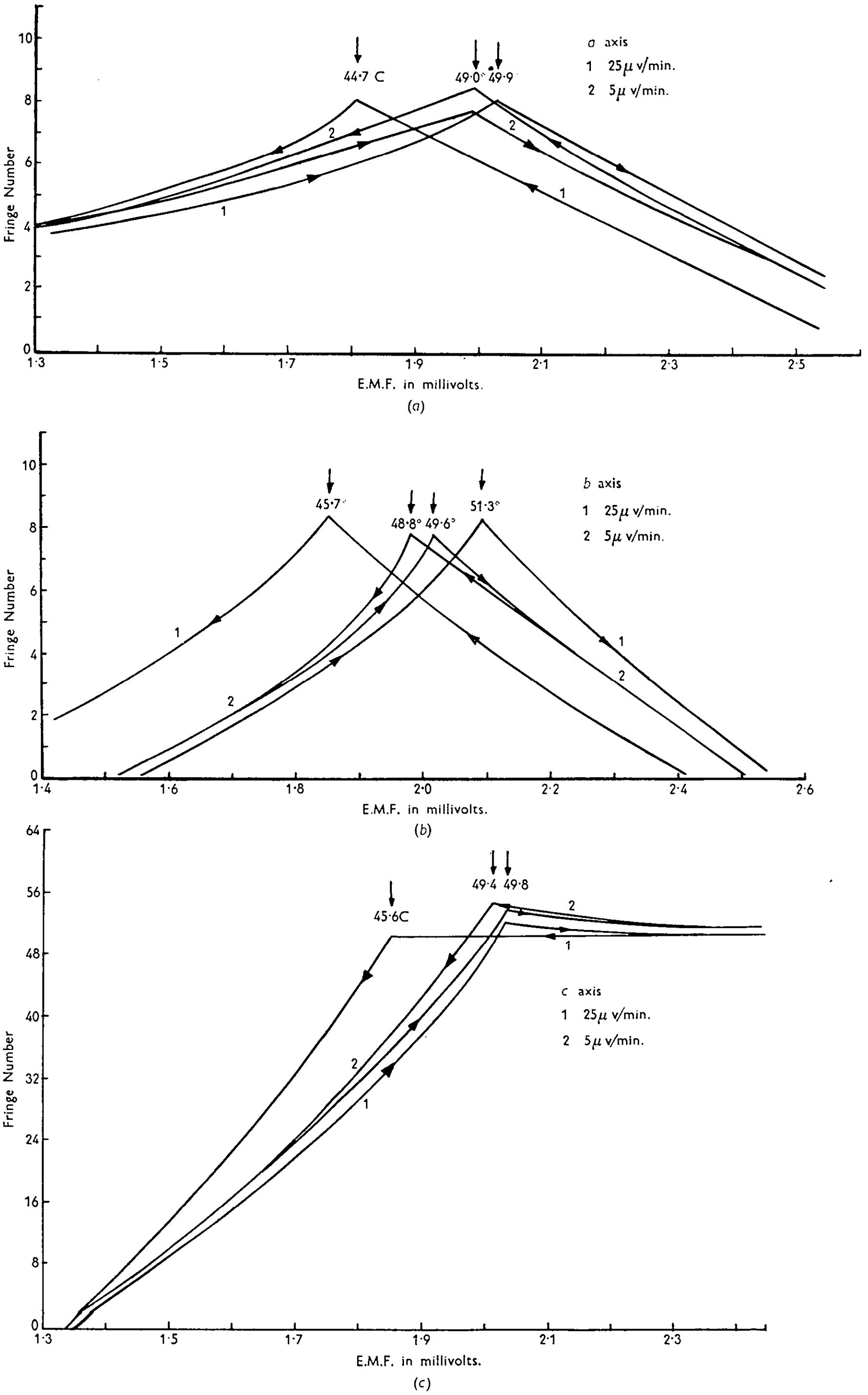
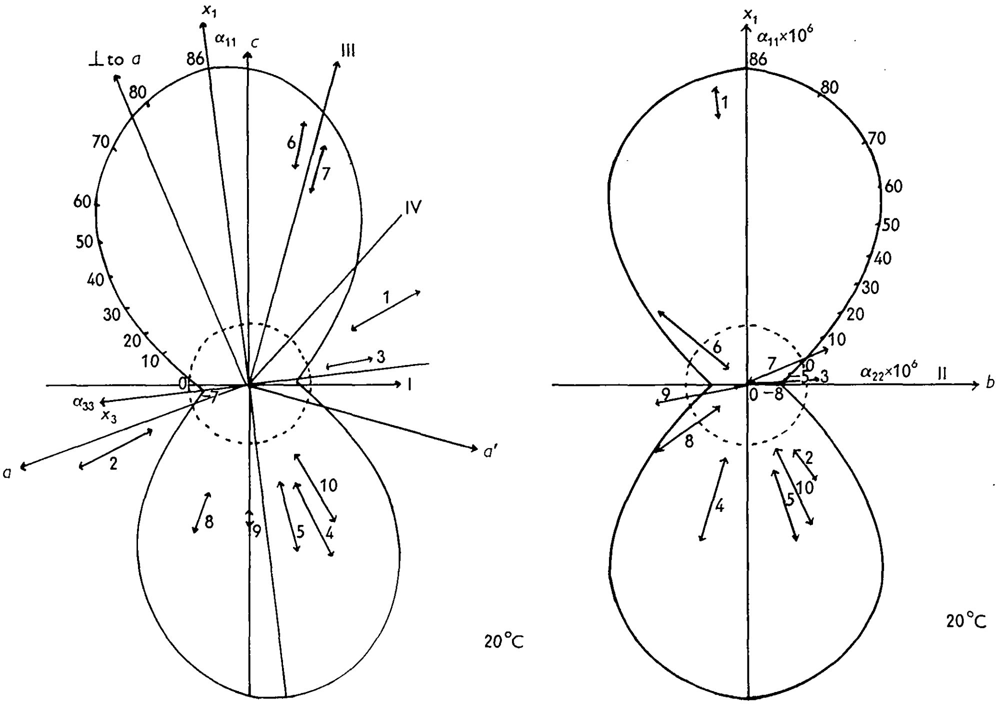


Fig. 2. (*a*) Thermal hysteresis versus rate of heating in triglycine sulphate along *a*-axis. (*b*) Thermal hysteresis versus rate of heating in triglycine sulphate along *b*-axis. (*c*) Thermal hysteresis versus rate of heating in triglycine sulphate along *c*-axis.

and 5 μv/min. Since the copper–constantan thermocouple reads 40 μv/degree, the rates of heating and cooling are about 0·6 deg./min., 0·4 deg./min. and 0·1 deg./min. respectively. In Figs. 2(*a*), 2(*b*) and 2(*c*), the number of the fringe in transit is plotted as a function of e.m.f. of the thermocouple near the transition point on an extended scale, for the two extreme rates of heating. It is seen from the figures that

(1) the difference in the temperatures of transition while heating and cooling decreases as the rate of



(a) (b)

Fig. 3. (a) Polar diagram of the expansion coefficient of triglycine sulphate in the *ac* plane with the projection of hydrogen bonds. (b) Polar diagram of the expansion coefficient of triglycine sulphate in the box_1 plane with the projection of hydrogen bonds.

heating is reduced and for 5 μv/min. the two points coincide to within 0·5 °C.,

(2) the width of the hysteresis loop decreases with the rate of heating and for the smallest rate of heating the loop is narrow.

These observations clearly indicate that as the rate of heating tends to zero, the hysteresis also tends to zero.

Polar diagram

Using the formula given by Wooster (1949), the maximum and minimum expansion coefficients α_{11} and α_{33} and ψ the angle that the direction of maximum expansion makes with the *c*-axis have been calculated. The expansion coefficients in the *ac* plane and box_1 plane (ox_1 is the direction of α_{11}) at 20 °C. are shown in the polar diagrams (Figs. 3(*a*) and 3(*b*)). The dashed circle represents zero expansion. Within the circle the expansion is negative and outside the circle the expansion is positive. The directions of *c* and *a*, ox_1 and ox_3 of α_{11} and α_{33} respectively and the axis *a′* of Wood & Holden are marked in the Fig.

It is well known that in ferroelectric crystals containing hydrogen bonds, the expansion coefficient in any direction is closely related to the direction of the hydrogen bonds (Ubbelohde & Woodward, 1946, 1957). The various hydrogen bonds with their lengths as given by Hoshino *et al.* (1959) are given in the following Table.

Bond number	Length	Bond number	Length
1	2·540 Å	6	2·879 Å
2	2·745	7	2·941
3	2·717	8	2·644
4	2·823	9	2·853
5	2·438	10	2·910

Of all the hydrogen bonds mentioned above, bond No. 5 with length 2·438 Å is said to be responsible for the switching mechanism (Hoshino, 1959). For a bond of such a short length, the hydrogen must be at the centre of the bond (Nakamoto, Margoshes & Rundle, 1955). But here the hydrogen is shown to be closely allied with the planar glycinium in the polarization state. If an electric field is applied the hydrogen switches over to the glycine, making it glycinium with the consequent changes in the NH_3 positions in the two ions. Thus the roles of the two ions are interchanged. This ‘flipping’ produces changes in other parts leading to a reversal of polarization.

The components of the various hydrogen bonds in the *ac* and box_1 planes are drawn in the polar diagram. The lengths of the arrows indicate the magnitude of the bonds. The shortest hydrogen bond of 2·438 Å lies along the direction of maximum expansion in both the *ac* and box_1 planes. But no such general rule holds for the other short hydrogen bonds in this crystal. Ubbelohde and his coworkers have investigated a large number of crystals, some with co-operative hydrogen bonds and some where the bonds do not provide the framework of the crystal. Only in crystals of the first type did they find the thermal expansion a maximum along the direction of the short hydrogen bonds (Rochelle salt, potassium dihydrogen phosphate, oxalic acid). In crystals of the other type such a correlation is not present (furoic acid). In view of the fact that triglycine sulphate is held by a network of hydrogen bonds, it is noteworthy that such a correlation between bond length and maximum expansion direction is not present except for the shortest hydrogen bond. Above the transition temperature all the bonds in the *ac* plane contract. The shortest hydrogen bond then contracts in length.

It is tempting to offer an explanation for the onset of ferroelectricity in terms of changes in the shortest hydrogen bond length. It is well known (Nakamoto, Margoshes & Rundle, 1955; Coulson, 1957) that the hydrogen will be at the centre of the bond if the hydrogen bond length is short i.e., $<2{\cdot}45$ Å. When the bond length increases, the hydrogen will occupy one of the two positions shifted from the centre. If the hydrogen atom is assumed to be at the centre of the bond above the transition point, then cooling the crystal should cause the bond to become larger. This causes a shift in the position of the hydrogen in the bond, with the attendant rotation of the glycinium I and SO_4 ions and the appearance of a spontaneous polarization. But now, from the results of thermal expansion, cooling the crystal further, below the transition point, causes the bond to contract, so that at a certain temperature the crystal should again become non-polar. In short the crystal should behave as Rochelle salt and exhibit two Curie points. But as no lower Curie point has been found for this crystal, such an explanation cannot therefore hold. Thus it seems that the peculiar nature of the thermal expansion of this crystal cannot by itself account for the onset of ferroelectricity.

The expansion of this crystal has been measured by Ezhkova *et al.* (1959) using the X-ray method. Employing the axes of Wood & Holden they measured the lattice spacings of [100], [010], [001] and [101] planes at different temperatures between 25 and 75 °C. These directions are marked I, II, III and IV in the polar diagram. They found *d*[001] to increase with temperature below the transition point. At the transition point there is a kink and *d*[001] starts decreasing above the transition point. The corresponding expansion coefficient α_{III} is positive and increases rapidly with temperature upto the transition temperature. It is also seen from the polar diagram obtained in the present study. Along the *b*-axis, they found the interplanar distance *d*[010] to expand from 25° to 75°. The expansion coefficient α_{II} is positive but shows a kink only at the transition point. This result is in direct contradiction with the result reported here. The measurements made by the author clearly show that α_{II} is negative below and becomes positive above the Curie point. This fact is confirmed by the sign reversal because the fringes reverse their direction of movement at the transition temperature. The interplanar distance *d*[100] contracts first up to the transition point and expands above the transition point in Ezhkova's work (1959). From the polar diagram it is obvious that at 20 °C., α_{I} is negative and small and so *d*[100] does contract at 20 °C. But as the temperature is raised α_{I} should become positive even below the Curie point because the crystal expands along the *a*-axis now. At the Curie point α_{I} should show a sudden reversal of sign and become negative. The discrepancy between the results obtained from X-ray measurements and expansion measurement may be explained in the light of a paper by Chynoweth (1959). He has reported changes in the ferroelectric properties of the crystal of triglycine sulphate, when it is subjected to ionizing radiation (X-rays and electrons). He has also shown that even a small X-ray dosage is sufficient to produce large changes in the ferroelectric properties, while for crystallographic structure determination one has to use large X-ray dosage. The radiation damage produced by X-rays might have profoundly influenced the lattice-spacing measurements of this crystal. In crystals where the variation of thermal expansion with temperature is complicated the interferometric method has the advantage over the X-ray method in that the progress of the expansion can be continuously observed.

The author expresses his grateful thanks to Prof. R. S. Krishnan for his keen interest in this work and for all facilities provided and to Dr R. Srinivasan for valuable suggestions and discussions. He is also grateful to Dr Vedam at whose suggestion these investigations were made.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1962). **15**, 87

The crystal structures of caesium, ammonium and potassium pertechnetates.

By B. J. MCDONALD and GWYNETH J. TYSON, *U.K.A.E.A., Production Group, Technical Branch, Windscale and Calder Works, Sellafield, Seascale, Cumberland, England*

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The crystal structures of caesium, ammonium and potassium pertechnetates have been determined from powder photographs. The preparation of these compounds is reported by Boyd (1959). He states that the ammonium and potassium salts are isomorphous with the corresponding perrhenates and have the tetragonal $CaWO_4$ structure.

The structures of ammonium and potassium pertechnetate were confirmed as tetragonal, space group $I4_1/a$, $CaWO_4$ type. The lattice parameters were found to be $a_0 = 5{\cdot}790$, $c_0 = 13{\cdot}310$ Å for NH_4TcO_4 and $a_0 = 5{\cdot}654$, $c_0 = 13{\cdot}030$ Å for $KTcO_4$.

The structure of $CsTcO_4$ was found to be orthorhombic with lattice parameters

$$a_0 = 5{\cdot}718,\ b_0 = 5{\cdot}918,\ c_0 = 14{\cdot}304\ \text{Å}\ .$$

The space group is *Pnma* and the metal atoms are in special position (*c*) $\pm(x, \frac{1}{4}, z;\ x+\frac{1}{2}, \frac{1}{4}, \frac{1}{2}-z)$ with $x = 0{\cdot}03$, $z = \frac{1}{8}$ for the 4 Cs ions and $x = 0{\cdot}97$, $z = \frac{5}{8}$ for the 4 Tc atoms (the Tc atom being at the centre of the tetrahedral TcO_4^- ion). The structure was found to be isomorphous with caesium perrhenate and caesium periodate. Table 1 shows the agreement between observed and calculated intensities for the first twenty lines of the pattern, neglecting the contribution of the oxygen atoms. The values of 0·03 and 0·97 for the x parameter are not very accurate because changes in the parameter have little effect on the calculated intensities. Table 2 illustrates the effect of varying x from 0 to 0·05 for Cs and from 0·95 to 1·0 for Tc, on the intensities of several lines.

Table 1. *Observed and calculated intensities for* $CsTcO_4$

hkl	*d* (obs.)	*d* (calc.)	*I* (obs.)	*I* (calc.)
111	3·959 Å	3·953 Å	15	0·28
004	3·576	3·576	100	100
113	3·121	3·127	5	5
020	2·959	2·959	60	62
200	2·859	2·859	50	49
022	2·736	2·734	5	0
121	2·582	2·585	10	1·4
203	2·460	2·459	1	0·09
115	2·353	2·348	5	3
024	2·285	2·280	60	60
204	2·236	2·233	50	49
116	2·067	2·062	80	86
221	2·038	2·035	5	6
125	1·937	1·935	1	0·65
223	1·893	1·891	1	0·09
026	1·850	1·856	1	0
132	1·804	1·804	50	56
224	1·787	1·783	50	49
312	1·758	1·759	40	38
313	1·697	1·698	5	7

We should like to thank J. R. Embleton for preparation of the compounds and useful discussions.

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Table 2. *Variation of line intensities with x parameter*

		I (calc.)					
hkl	*I* (obs.)	$x_{Cs} = 0$ $x_{Tc} = 1$	$x_{Cs} = 0{\cdot}01$ $x_{Tc} = 0{\cdot}99$	$x_{Cs} = 0{\cdot}02$ $x_{Tc} = 0{\cdot}98$	$x_{Cs} = 0{\cdot}03$ $x_{Tc} = 0{\cdot}97$	$x_{Cs} = 0{\cdot}04$ $x_{Tc} = 0{\cdot}96$	$x_{Cs} = 0{\cdot}05$ $x_{Tc} = 0{\cdot}95$
116	80	89	89	88	86	84	81
132	50	58	58	57	56	55	53
224	50	56	55	53	49	43	38
200	50	56	55	53	49	43	37
312	40	54	52	46	38	29	19
313	5	0	0·85	3	7	11	16