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Crystallographic data on some sodium phosphorothioates.

By D. P. Elias, *Research Department, Albright and Wilson (Mfg.) Limited, Oldbury, Birmingham, England*

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Sulphur can replace oxygen in the orthophosphate anion PO_4^{3-} to form the phosphorothioate anions PSO_3^{3-}, $PS_2O_2^{3-}$, PS_3O^{3-} and PS_4^{3-}. The series of phosphorothioates can be obtained as sodium salts, the crystals of which are all hydrated and generally hygroscopic (Glatzel, 1905; Klement, 1947; Neogi & Ghosh, 1929; Wurtz, 1847).

With the exceptions of the structural investigation of cuprous phosphorotetrathioate Cu_3PS_4 (Ferrari & Cavalca, 1948) and the determination of the space group and unit cell data on potassium OO-diethyl phosphorothioate $(C_2H_5O)_2POSK$ (Rollet, 1954), published crystallographic data on phosphorothioates are lacking, and so unit-cell and space-group data have been obtained for the sodium salts shown in Table 1.

Cell dimensions were measured from rotation photographs and space-group absences were determined from zero- and first-layer Weissenberg photographs taken about the principal axes.

Goniometric measurements are recorded for trisodium phosphorothioate only (de la Provostaye, 1847); these are in agreement with the X-ray measurements when c/a (X-ray) $\equiv 4c/a$ (goniometric), taking the hexagonal unit cell as basis.

The space-group possibilities for trisodium phosphorothioate require the anion to have at least three-fold symmetry. In the remaining salts special symmetry is not imposed by space-group considerations.

X-ray powder photographs of trisodium phosphorodithioate and trisodium phosphorotrithioate confirm the isomorphism suggested by the similarities in their unit-cell constants. Mixed-crystal formation is known to occur between these two salts (Klement, 1947), and the low value observed for the density of trisodium phosphorotrithioate may thus be accounted for, but the crystals of trisodium phosphorotrithioate are poorly formed and have a powdery texture.

Crystals of form I of trisodium phosphorotetrathioate appear to be always twinned; for this reason more accurate measurements of [a] and β were not possible.

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Table 1. *Crystallographic data*

Compound	System	Space group	a (Å)	b (Å)	c (Å)		Density (g.cm.$^{-3}$) Obs.	Calc.	Z
Trisodium phosphorothioate, $Na_3PSO_3.12\,H_2O$	Rhombohedral	$R\bar{3}m$ or $R32$ or $R3m$	12·58	—	—	$\alpha = 42{\cdot}3°$	1·58	1·61	2
Trisodium phosphorodithioate, $Na_3PS_2O_2.11\,H_2O$	Orthorhombic	$Pnma$ or $Pn2_1a$	12·51	13·94	9·48	—	1·58	1·58	4
Trisodium phosphorotrithioate, $Na_3PS_3O.11\,H_2O$	Orthorhombic	$Pnma$ or $Pn2_1a$	12·60	14·02	9·33	—	1·60	1·65	4
Trisodium phosphorotetrathioate, $Na_3PS_4.8\,H_2O$ I	Monoclinic	$P2_1/c$	14·7	7·09	14·15	$\beta = 92°$	1·67	1·68	4
$Na_3PS_4.8\,H_2O$ II	Monoclinic	$P2_1/a$	13·62	12·83	8·69	$\beta = 104{\cdot}0°$	1·67	1·68	4

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Ferroelectricity in ammonium monochloroacetate.*

By R. Pepinsky, Y. Okaya and T. Mitsui, *X-Ray and Crystal Analysis Laboratory, Department of Physics, The Pennsylvania State University, University Park, Pa., U.S.A.*

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Ammonium monochloroacetate is dimorphous at room temperature. Form I is orthorhombic, space group $P2_12_12_1$, with $a = 5{\cdot}71$, $b = 7{\cdot}31$, $c = 12{\cdot}08$ Å, $\varrho_o = 1{\cdot}460$ g.cm.$^{-3}$, and 4 molecules per cell. Form II is monoclinic, space group $C2/c$, with $a = 8{\cdot}42$, $b = 11{\cdot}63$, $c = 9{\cdot}82$ Å, $\beta = 110°$, $\varrho_o = 1{\cdot}558_5$ g.cm.$^{-3}$, and 8 molecules per cell. Both forms appear in the same crystallization, often, when the compound is prepared under

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anhydrous conditions, in the cold, by passing dry NH_3 gas into water-free chloroacetic acid dissolved in freshly-distilled absolute ethyl alcohol. Form I can be prepared from cold aqueous solutions (a rise in temperature leads to hydrolysis and a number of unwanted products). Form II was obtained only once from cold aqueous solution, and we have not been able to repeat the experiment.

Form II shows a dielectric anomaly at −150° C. The dielectric constant along b is 5 at room temperature, and reaches a maximum of 15 at −150° C. Below this temperature the crystals show spontaneous polarization and ferroelectric hysteresis. The coercive field is ~ 10 kV.cm.$^{-1}$ at −170° C. The spontaneous polarization is in the neighborhood of 0·1 microcoul.cm.$^{-2}$. The observed hysteresis loops are often unsymmetric. The transition is apparently of first order. The symmetry of the low-temperature phase is apparently $C2$, the glide plane of the upper phase disappearing as does the mirror plane in the case of triglycine sulfate and isomorphs (Pepinsky, Okaya & Jona, 1957) and in ferroelectric silver glycinate (Pepinsky, Eastman & Mitsui, 1957).

The crystal structure of the room-temperature phase of Form II is under X-ray examination.

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A method of correcting the primary extinction effect in electron diffraction.

By Sigemaro Nagakura, *Tokyo Institute of Technology, Oh-okayama, Meguroku, Tokyo, Japan*

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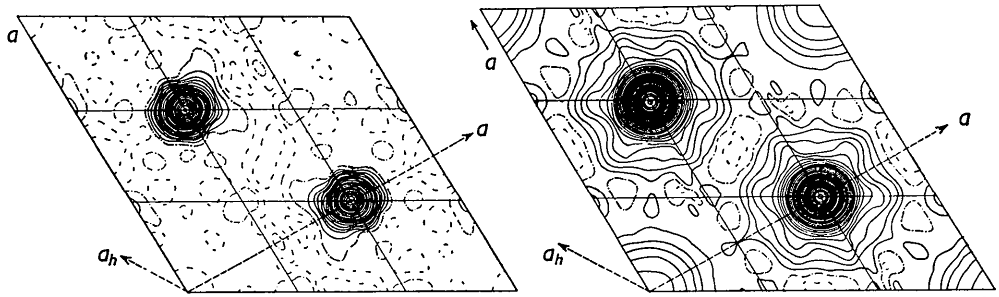
A serious difficulty in applying the electron-diffraction method to crystal structure analysis arises from the effect of primary extinction or dynamical diffraction. Although Pinsker (1949) and Jamzin (1949) held that the effect is not significant in practice, Lennander (1954) and Kuwabara (1957) showed that the effect is hardly negligible. Recently, Honjo & Kitamura (1957) showed that the variation of diffraction intensity with wavelength is in accordance, at least approximately, with the theory of primary extinction given by Blackman (1939), and they proposed a method to eliminate the effect by extrapolating the observed intensity to zero wavelength. The present author proposes another method to correct the primary extinction effect, utilizing Wilson's intensity statistics (Wilson, 1949) combined with the theory of primary extinction. This paper describes briefly the method, with the result of its application to the structure analysis of nickel carbide, Ni_3C.

Electron-diffraction patterns of Ni_3C suggest that the structure belongs to the space group $R\bar{3}c$. Nickel atoms are in 18(e) positions with $x = \frac{1}{3}$ and carbon atoms in 6(b) positions (Nagakura, 1957). Fig. 1(a) shows the two-dimensional Fourier map of the carbide calculated by assuming that the observed intensity $I_{\text{obs.}}$ is proportional to the square of the structure amplitude F for electrons. The intensity data were obtained from powder patterns taken with 40 kV. electrons (wavelength $\lambda = 0{\cdot}06$ Å). While nickel peaks appear in reasonable positions corresponding to a close-packed hexagonal arrangement (Jacobson & Westgren, 1933), there is no indication of carbon peaks in spite of the fact that the scattering amplitude of carbon atoms for electrons is as large as one-third of that of nickel atoms. The fact that carbon atoms did not appear on the map is due to the primary extinction effect participating strongly in the diffraction intensity, as shown below.



(a) (b)

Fig. 1. (a) Two-dimensional Fourier map of Ni_3C synthesized from uncorrected intensity data. The map shows a part of the basal-plane projection, corresponding to Jacobson & Westgren's unit cell (Nagakura, 1957). The contours are drawn at arbitrary intervals. (b) Two-dimensional Fourier map of Ni_3C synthesized from the final values of the corrected intensity. The contours are drawn at intervals of 0·5 V.Å^{-2}. The chain lines indicate zero level and the broken lines negative regions.