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The Crystal Structure of Tetra-*n*-propyl Ammonium Bromide*

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$(n\text{-}C_3H_7)_4NBr$ crystallizes in the tetragonal space group $I\bar{4}$. The cell constants are $a = 8{\cdot}24$, $c = 10{\cdot}92$ Å, with two molecules per unit cell. The ions pack in the cubic zinc sulphide-type arrangement, where each Br^- ion is surrounded by a tetrahedron of $(n\text{-}C_3H_7)_4N^+$ ions and vice versa. The carbons and nitrogen are clearly resolved in a Fourier projection on the (001) plane, and the parameters of these atoms were refined by a least-squares treatment of the three-dimensional data. Bond distances were calculated giving two C–C bonds of 1·56 and 1·54 Å and a C–N bond length of 1·55 Å.

Introduction

$(n\text{-}C_3H_7)_4NBr$ was one of a series of tetra-alkyl ammonium halides whose physical properties were being investigated. The crystal structure was undertaken with a view to studying the packing arrangements in these compounds.

The material was synthesized by Dr E. R. Bissell at this laboratory by reacting tri-*n*-propyl amine with *n*-propyl bromide in an ethanol solution. The resulting product was recrystallized from ethanol and vacuum-dried.

Experimental

Single-crystal Weissenberg equi-inclination patterns were photographed of layers zero through four about an *a*-axis rotation. The X-ray wave length used throughout was Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å; this was obtained by filtering the primary beam of a Cu tube with a 0·001 in. nickel foil.

Intensities were measured by visually comparing the diffraction intensities with a calibrated scale of exposures. The intensities from different layer-line films were normalized with respect to each other by the use of equivalent reflections that appeared on more than one layer. The intensities were corrected for the Lorentz, polarization and velocity factor corrections.

A visual perusal of the films indicates significant absorption effects; owing to the complexity of such a calculation, these were not corrected for.

Cell constants and space group

The cell constants of the body-centered tetragonal cell, as calculated from the Weissenberg single-crystal photographs, are:

$$a = 8{\cdot}24 \pm 0{\cdot}01,\quad c = 10{\cdot}92 \pm 0{\cdot}01 \text{ Å}.$$

There are two molecules per unit cell, $Z = 2$, giving a calculated X-ray density of $1{\cdot}192 \pm 0{\cdot}003$ g.cm.$^{-3}$.

The space group is $I\bar{4}$ and was determined as follows: The only regular extinctions observed were the body-centered ones; this, plus the observation that the intensities from hkl and $\bar{h}kl$ reflections were not equivalent, led to the three possible space groups $I4$, $I\bar{4}$, and $I4/m$. Only $I\bar{4}$ among these fulfills the requirements of being able to accommodate the tetrahedral configuration expected for the tetra-*n*-propyl ammonium ion.

The bromine and nitrogen atoms must occupy special twofold positions, and the carbon atoms must occupy three sets of general eightfold positions. Although the space group itself is non-centric, the projection on the (001) plane is centric. By placing the heavy bromine ion at the special position 0, 0, 0

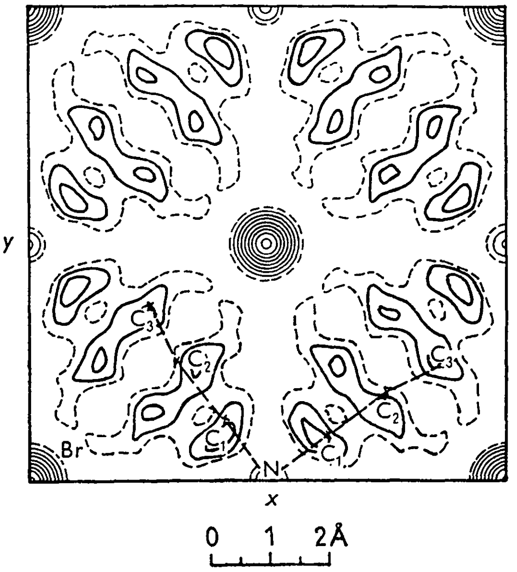

Fig. 1. Electron-density projection on the (001) plane. Contours are in arbitrary units with the zero level indicated by a broken contour. The contours of the bromine atom at the origin and center are spaced with one-fourth the frequency used in the lighter atoms. The crosses indicate the final positions after the least-squares refinement.

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all of the F_{hk0} phase angles can be taken as zero for a first approximation. A Fourier summation of the electron-density projection was calculated, using 32 $hk0$ reflections with all the signs taken positive. The result is shown in Fig. 1; the nitrogen and carbon atoms are clearly resolved. The atomic positions are as follows:

Br^-	2(a)	0, 0, 0; + body centering,
N	2(c)	$\frac{1}{2}$, 0, $\frac{1}{4}$; + body centering,
C_1	8(g)	$x, y, z;\ \bar{x}, \bar{y}, z;\ y, \bar{x}, \bar{z};\ \bar{y}, x, \bar{z};$ + body centering,
C_2	8(g)	$x, y, z;\ \bar{x}, \bar{y}, z;\ y, \bar{x}, \bar{z};\ \bar{y}, x, \bar{z};$ + body centering,
C_3	8(g)	$x, y, z;\ \bar{x}, \bar{y}, z;\ y, \bar{x}, \bar{z};\ \bar{y}, x, \bar{z};$ + body centering.

The complete three-dimensional data consisting of 313 independent non-zero intensities were then subjected to a least-squares treatment. A set of trial x and y parameters for the carbon atoms were obtained from the projection in Fig. 1; trial z parameters were calculated from estimated bond lengths. Hydrogen positions were not included. Independent isotropic temperature factors were included and refined by the computations. Eight least-squares refinements were done with the aid of the IBM 650 computer. The final atomic parameters for the carbon atoms and their standard deviations are shown in Table 1. The standard deviations indicated are estimated by the method described by Cruickshank (1949).

Table 1. *Final atomic parameters for the carbon atoms*

	x	y	z
C_1	0·413 ± 0·004	0·121 ± 0·004	0·163 ± 0·003
C_2	0·311 ± 0·004	0·249 ± 0·005	0·231 ± 0·004
C_3	0·246 ± 0·006	0·367 ± 0·006	0·131 ± 0·004

The temperature factor used in the calculations was $\exp(-B/\lambda^2 . \sin^2\theta)$; the resultant values of B after refinement by the least-squares treatment are shown in Table 2.

Table 2. *Isotropic temperature factors*

	B (Å^2)
Br	2·6
N	2·6
C_1	3·6
C_2	4·3
C_3	5·8

The interatomic distances and angles calculated for the propyl-ammonium ion are shown in Fig. 2. The standard deviations of the bond lengths in Fig. 2 are calculated from the standard deviations of the parameters in Table 1 by the method suggested by Cruickshank & Robertson (1953).

The reliability factors are as follows:

$$R_1 = \Sigma|F_o - F_c| \div \Sigma F_o = 0{\cdot}177\ ,$$
$$R_2 = \sqrt{\{\Sigma|F_o - F_c|^2 \div \Sigma|F_o|^2\}} = 0{\cdot}207\ .$$

In the least-squares refinement, $(R_2)^2$ is the quantity whose value is minimized. The observed and calculated structure factors are listed in Table 3; the reflections are arranged in order of increasing diffraction angle. The scale factor relating the observed to calculated structure factors was included as a variable and refined by the least-squares calculations. Carbon and nitrogen scattering factors were taken from the calculations of Hoerni & Ibers (1954); the bromine values were taken from the *Internationale Tabellen* (1935).

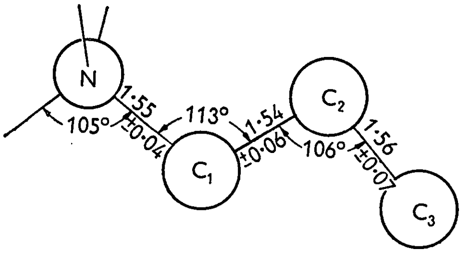

Fig. 2. Interatomic distances (Å) and angles.

Discussion

A sketch of the packing in the crystal structure is shown in Fig. 3; for simplicity the carbon skeleton is shown without hydrogen atoms. Each tetra-n-propyl ammonium ion is surrounded by a tetrahedron of bromide ions and vice versa. This is the ZnS-type arrangement; a face-centered tetragonal lattice consisting of the [110], [$\bar{1}$10] and [001] axes of the body-centered cell is a cell with $c/a = 0{\cdot}965$ and is comparable to the face-centered cubic ZnS-type cell. The bromide ion is surrounded by 4 methyl and 8 methylene groups with the following distances:

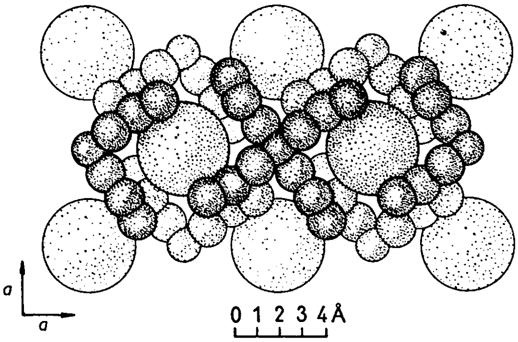

Fig. 3. Packing in the structure.

Br–4 $CH_2(C_1)$ 3·96 Å ,
Br–4 $CH_2(C_2)$ 3·92 Å ,
Br–4 $CH_3(C_3)$ 3·91 Å .

These distances are comparable to a calculated distance of 3·95 Å, assuming a radii of 2·0 Å for a methyl and a methylene group and 1·95 Å for bromide (Pauling, 1948).

Table 3. *Observed and calculated structure factors*

h k ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k ℓ	$\lvert F_o \rvert$	$\lvert F_c \rvert$
1 0 1	35	50	5 1 0	23	33	5 4 1	34	26	5 4 5	21	16	8 1 3	20	18	8 4 2	9	11	9 0 5	5	10
1 1 0	16	19	$\bar{5}$ 1 0	25	25	6 1 3	20	20	4 2 8	19	19	7 4 3	21	17	5 110		11	6 210	7	9
0 0 2	14	8	3 3 4	31	24	$\bar{6}$ 1 3	20	20	$\bar{4}$ 2 8	19	18	$\bar{7}$ 4 3	18	15	$\bar{5}$ 110	7	11	$\bar{6}$ 210	7	9
2 0 0	15	21	3 2 5	30	27	6 2 2	20	18	6 0 6	10	12	8 2 2	9	10	6 1 9	7	10	1 013	5	9
1 1 2	48	68	$\bar{3}$ 2 5	28	27	$\bar{6}$ 2 2	18	16	0 010	*	7	$\bar{8}$ 2 2	9	11	$\bar{6}$ 1 9	13	15	9 4 1	*	9
2 1 1	42	49	5 1 2	22	29	5 3 4	19	19	5 2 7	10	11	5 3 8	10	12	1 112	*	8	$\bar{9}$ 4 1	*	8
$\bar{2}$ 1 1	42	58	$\bar{5}$ 1 2	23	22	$\bar{5}$ 3 4	22	17	$\bar{5}$ 2 7	17	16	$\bar{5}$ 3 8	14	12	9 1 2	15	16	4 012	*	8
1 0 3	42	52	2 2 6	17	17	5 2 5	24	24	7 3 0	10	8	7 1 6	8	12	$\bar{9}$ 1 2	7	10	7 2 9	*	10
2 0 2	46	51	1 0 7	19	23	$\bar{5}$ 2 5	22	19	$\bar{7}$ 3 0	20	16	$\bar{7}$ 1 6	13	17	8 0 6	9	11	$\bar{7}$ 2 9	*	7
2 2 0	55	63	4 2 4	28	25	2 2 8	25	25	7 2 3	17	17	4 3 9	14	14	9 2 1	8	9	9 3 4	*	9
0 0 4	22	31	$\bar{4}$ 2 4	25	22	4 1 7	17	17	$\bar{7}$ 2 3	10	11	$\bar{4}$ 3 9	10	14	$\bar{9}$ 2 1	11	11	$\bar{9}$ 3 4	*	6
3 0 1	31	40	5 2 1	21	20	$\bar{4}$ 1 7	25	23	1 110	19	20	5 0 9	7	11	4 111	6	10	9 2 5	6	9
3 1 0	29	32	$\bar{5}$ 2 1	34	26	6 0 4	20	24	3 2 9	10	9	6 0 8	12	14	$\bar{4}$ 111	6	13	$\bar{9}$ 2 5	*	8
$\bar{3}$ 1 0	42	41	5 0 3	26	24	6 3 1	24	22	$\bar{3}$ 2 9	22	19	6 4 6	10	11	2 012	12	13	3 312	*	7
2 1 3	30	34	4 3 3	25	24	$\bar{6}$ 3 1	24	16	7 1 4	14	17	$\bar{6}$ 4 6	18	14	9 0 3	6	9	10 0 0	*	10
$\bar{2}$ 1 3	23	22	$\bar{4}$ 3 3	19	14	5 4 3	29	22	$\bar{7}$ 1 4	8	10	4 010	7	13	7 1 8	*	10	8 0 8	8	10
2 2 2	28	23	3 1 6	29	29	$\bar{5}$ 4 3	25	19	6 3 5	25	18	6 3 7	17	15	$\bar{7}$ 1 8	6	9	8 4 6	*	8
1 1 4	33	39	$\bar{3}$ 1 6	34	32	3 1 8	13	14	$\bar{6}$ 3 5	18	14	$\bar{6}$ 3 7	14	12	5 4 9	9	10	$\bar{8}$ 4 6	*	8
3 1 2	29	33	4 1 5	26	31	$\bar{3}$ 1 8	20	20	7 3 2	23	20	8 0 4	7	12	$\bar{5}$ 4 9	13	11	$\bar{8}$ 3 7	7	8
$\bar{3}$ 1 2	43	43	$\bar{4}$ 1 5	24	24	5 1 6	26	30	$\bar{7}$ 3 2	23	15	8 3 1	14	14	8 3 5	8	11	$\bar{2}$ 113	10	11
2 0 4	29	33	4 4 0	33	25	$\bar{5}$ 1 6	22	20	6 2 6	10	11	$\bar{8}$ 3 1	17	13	$\bar{8}$ 3 5	8	10	10 1 1	*	10
3 2 1	48	39	2 1 7	22	27	1 0 9	16	17	$\bar{6}$ 2 6	16	15	2 111	7	11	6 4 8	9	13	$\bar{10}$ 1 1	*	9
$\bar{3}$ 2 1	26	26	$\bar{2}$ 1 7	22	23	6 2 4	23	22	2 1 0	10	14	$\bar{2}$ 111	11	12	$\bar{6}$ 4 8	15	12	4 212	*	7
3 0 3	31	32	5 3 0	22	23	$\bar{6}$ 2 4	23	19	6 4 4	18	16	3 310	14	14	8 2 6	8	10	$\bar{4}$ 212	*	9
1 0 5	29	33	$\bar{5}$ 3 0	22	11	7 0 1	13	18	$\bar{6}$ 4 4	18	14	5 2 9	13	15	$\bar{8}$ 2 6	8	8	9 4 3	*	9
4 0 0	29	32	5 2 3	26	26	7 1 0	17	20	5 1 8	8	12	$\bar{5}$ 2 9	13	14	4 410	9	8	$\bar{9}$ 4 3	10	9
2 2 4	46	45	$\bar{5}$ 2 3	28	22	$\bar{7}$ 1 0	11	12	$\bar{5}$ 1 8	8	11	6 2 8	15	14	8 4 4	9	11	10 0 2	*	7
4 1 1	26	27	4 4 2	26	17	6 3 3	17	14	4 1 9	13	15	$\bar{6}$ 2 8	13	13	$\bar{8}$ 4 4	9	10	9 1 6	*	8
$\bar{4}$ 1 1	31	33	$\bar{5}$ 1 4	39	27	$\bar{6}$ 3 3	35	23	$\bar{4}$ 1 9	11	9	4 210	9	12	2 212	8	11	$\bar{9}$ 1 6	5	8
3 3 0	40	24	6 0 0	16	17	2 1 9	15	20	7 0 5	13	17	$\bar{4}$ 210	9	11	9 3 0	8	8	$\bar{10}$ 2 0	5	8
3 2 3	33	28	5 3 2	10	21	$\bar{2}$ 1 9	15	60	8 0 0	19	20	7 0 7	7	12	9 2 3	8	10	8 2 8	*	8
$\bar{3}$ 2 3	60	54	$\bar{5}$ 3 2	44	30	6 1 5	11	17	2 210	9	12	8 2 4	12	13	$\bar{9}$ 2 3	8	8	3 013	*	8
4 0 2	25	27	0 0 8	25	31	$\bar{6}$ 1 5	15	16	6 1 7	8	15	$\bar{8}$ 2 4	12	15	5 310	*	10	6 111	*	8
3 1 4	27	32	4 0 6	16	13	6 4 0	30	24	$\bar{6}$ 1 7	11	13	3 011	7	9	$\bar{5}$ 310	11	13	$\bar{6}$ 111	4	6
$\bar{3}$ 1 4	14	14	3 0 7	19	26	$\bar{6}$ 4 0	35	28	8 1 1	11	13	$\bar{8}$ 3 3	9	11	6 3 9	*	7	10 113	4	7
2 1 5	19	21	6 1 1	16	21	7 1 2	11	14	$\bar{8}$ 1 1	8	11	7 3 6	9	14	$\bar{6}$ 3 9	*	8	$\bar{10}$ 113	4	8
2 1 5	33	39	$\bar{6}$ 1 1	20	22	$\bar{7}$ 1 2	20	24	7 4 1	11	11	$\bar{7}$ 3 6	9	10	9 1 4	*	8	$\bar{10}$ 2 2	5	8
4 2 0	32	27	6 0 2	19	22	4 0 8	23	22	$\bar{7}$ 4 1	15	13	7 4 5	14	12	$\bar{9}$ 1 4	6	10	7 110	*	8
$\bar{4}$ 2 0	34	35	1 1 8	18	19	4 4 6	21	17	8 0 2	10	16	$\bar{7}$ 4 5	14	11	3 112	*	11	$\bar{7}$ 110	6	10
3 3 2	46	34	3 3 6	29	23	4 3 7	18	18	3 110	11	15	8 1 5	7	11	$\bar{3}$ 112	8	8	5 112	*	8
0 0 6	25	31	4 3 5	19	19	$\bar{4}$ 3 7	18	16	$\bar{3}$ 110	15	15	$\bar{8}$ 1 5	7	10	$\bar{9}$ 3 2	11	11	$\bar{5}$ 112	4	9
4 1 3	29	34	$\bar{4}$ 3 5	34	25	5 0 7	21	21	7 3 4	10	15	8 4 0	10	10	6 010	5	10	6 410	*	6
$\bar{4}$ 1 3	28	27	5 0 5	25	21	7 2 1	17	17	$\bar{7}$ 3 4	17	14	$\bar{8}$ 4 0	13	11	8 1 7	*	9	$\bar{6}$ 410	*	5
4 2 2	35	31	6 2 0	18	19	$\bar{7}$ 2 1	25	20	7 2 5	*	7	7 2 7	8	13	$\bar{8}$ 1 7	*	8	9 0 7	5	8
$\bar{4}$ 2 2	31	27	$\bar{6}$ 2 0	25	25	7 0 3	13	14	$\bar{7}$ 2 5	13	15	$\bar{7}$ 2 7	12	13	7 4 7	*	6	3 213	*	7
1 1 6	21	25	2 0 8	17	16	6 4 2	15	15	8 2 0	16	17	9 0 1	9	11	$\bar{7}$ 4 7	14	10	3 213	*	6
3 0 5	24	27	4 2 6	20	16	$\bar{6}$ 4 2	15	11	$\bar{8}$ 2 0	13	13	3 211	12	13	4 311	*	9	10 0 4	5	9
2 0 6	29	31	$\bar{4}$ 2 6	22	21	3 3 8	18	14	4 4 8	*	12	$\bar{3}$ 211	8	12	4 311	*	8	10 3 1	5	8
4 0 4	38	39	3 2 7	30	28	5 3 6	18	17	5 4 7	15	15	0 012	11	14	5 011	8	10	$\bar{9}$ 3 6	9	11
4 3 1	33	28	$\bar{3}$ 2 7	13	13	$\bar{5}$ 3 6	18	16	$\bar{5}$ 4 7	15	15	9 1 0	12	4	7 3 8	*	7			
$\bar{4}$ 3 1	39	35	4 4 4	36	25	3 0 9	19	20	1 011	12	15	$\bar{9}$ 1 0	13	13	$\bar{7}$ 3 8	*	10			
5 0 1	27	28	5 4 1	24	19	5 4 5	11	16	8 1 3	11	14	8 4 2	9	11	7 0 9	*	8			

*Unobserved or zero observed reflections.

The hydrogen atoms on C_1 and C_2 carbons can be located specifically since they are bonded to carbon atoms that are themselves rigidly fixed by their bonding to two neighboring atoms.

Assuming 1·10 Å as the C–H bond length and a tetrahedral angle between the hydrogens bonded to the same carbon atom, the parameters for four hydrogens were calculated. Each of the four is in an eightfold general position similar to the carbon atoms. The derived positions are shown in Table 4.

On the basis of these positions some atomic distances were calculated and are summarized in Table 5. In the case of the C_3 atom, where the hydrogen positions were not calculated, the distances are calculated for that carbon as a CH_3 group to its nearest neighbors.

From the above table of distances, the apparent van der Waals radius of hydrogen with respect to hydrogen in this compound is between 1·06 and 1·09 Å; that of hydrogen with respect to the negative bromide ion is 0·89 and 1·03 Å.

Table 4. *Calculated hydrogen positions on carbons 1 and 2*

		x	*y*	*z*
C_1	H_1	0·332	0·051	0·012
	H_2	0·506	0·184	0·108
C_2	H_1	0·209	0·191	0·279
	H_2	0·387	0·316	0·297

Table 5. *Interatomic distances in tetra-n-propyl ammonium bromide*

	Br	–4 H	2·98 Å
		4 H	2·84
		4 $CH_3(C_3)$	3·91
	N	–4 C_1	1·56*
		8 H	2·17
	C_1	–1 C_1	1·56*
		1 C_2	1·54*
		2 H	1·10*
		2 H	2·18, 2·19
	C_2	1 C_1	1·54*
		1 C_3	1·55*
		2 H	1·10*
		2 H	2·16
	$C_3(CH_3)$	–1 C_2	1·55*
		2 H	2·19
		4 Br	3·91
C_1	H_1	–1 C_1	1·10* Å
		–1 H	1·81†
		–2 H	2·13, 2·35
	H_2	–1 C_1	1·10*
		–1 H	1·81†
		–1 C_2	2·16
		–2 H	2·15, 2·35
C_2	H_1	–1 C_2	1·10*
		–1 H	1·80†
		–1 C_3	2·19
		–1 H	2·15
	H_2	1 C_2	1·10*
		1 H	1·80†
		1 CH_3	2·19
		1 H	2·13

* Bonded, † Twin hydrogen.

The C–N bond length of 1·55±0·04 Å can be compared with the calculated value of 1·47 Å obtained by summing the covalent radii of tetrahedral nitrogen and carbon (Robertson, 1953). The tetrahedron is slightly distorted to accommodate the packing of these large ions.

I should like to thank Dr E. R. Bissell for providing the material; Mr V. Silveira for some of the calculations; Dr M. Senko for the use of his least-squares code; and Dr D. H. Templeton for his interest and suggestions.

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An Improved Electronic Flying-Spot Densitometer for Analyzing X-ray Photographs

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An improved flying-spot densitometer has been constructed for analyzing both wide-angle and small-angle X-ray films. Speed and convenience of measurement are the primary improvements, made possible by the use of a flat-face cathode-ray scanning tube and novel calibration methods. Provision for circular and line scans permits the measurement of optical density variations both azimuthally and radially in an X-ray photograph. Optical density profiles are plotted on a flat-face cathode-ray display tube. Permanent records of any profile can be made readily in 1 min. with an oscilloscope-record camera.

A measure of the crystallite orientation in fiber patterns can be obtained in less than 5 min. Curves of density versus radial distance can likewise be obtained in less than 5 min. from diffuse small-angle scattering diagrams. Other uses and modifications of the instrument are suggested.

Introduction

The flying-spot scanning densitometer to be described was built to fill a need for an instrument than can quickly and easily provide quantitative data for routine X-ray diffraction characterization of fibers. Two types of diagrams that have been analyzed with the flying-spot densitometer are discussed below. Several other uses of more general interest are suggested later.

The principle of scanning photometry is not new (Robertson & Dawton, 1941), but it has been possible to realize the full advantage of such an instrument only since the introduction of a tight-tolerance flat-face cathode-ray tube.

Wide angle X-ray diffraction patterns of crystalline fibers are similar to patterns of single crystals rotated about one crystallographic axis. For fibers, however, many of the individual crystallites may have imperfect alignment with respect to this axis, so that each diffraction spot becomes an arc. In general, the amount of orientation of these crystallites is quite variable, and arcs of different lengths appear. A measure of the amount of this orientation in a fiber is desired, since it is usually related to the process of fiber formation and to its physical properties. A convenient measure