

Conclusion

Cette différence entre les structures avec et sans centre de symétrie suggère quelques remarques à propos de la précision des coordonnées atomiques.

Quand il s'agit d'une structure centrosymétrique, on peut discuter directement la précision, en admettant qu'on connaît les $|F|$ à une erreur expérimentale près, car pour un petit déplacement Δr d'un atome les phases et la transformée de Fourier ne sont pas modifiées.

Le cas d'une structure non centrosymétrique est différent.

Imaginons une structure dont les positions atomiques r_i soient connues. Si on calcule la transformée de Fourier de la portion d'espace réciproque contenue dans une sphère limitée, avec les $|F|$ affectés par les erreurs expérimentales, et avec les angles des phases correspondant aux positions correctes, on retrouve les pics atomiques déplacés aux points $r_i + \epsilon_i$.

Si on calculait la transformée de Fourier sans limitation de l'espace réciproque, avec les $|F|$ corrects, et avec les angles des phases correspondant aux positions atomiques $r_i + 2\epsilon_i$ les pics devraient se trouver aux points $r_i + \epsilon_i$, à moitié chemin entre les positions correctes et les positions pour lesquelles on calcule les angles des phases.

D'autre part, la limitation de l'espace réciproque et les erreurs des $|F|$ produisent des déplacements ϵ_i .

En conséquence la transformée de Fourier calculée avec les $|F|$ incorrects, avec la limitation de l'espace réciproque, et avec les angles des phases correspondant aux positions $r_i + 2\epsilon_i$ laisse les pics atomiques aux mêmes points $r_i + 2\epsilon_i$. L'application réitérée des transformations de Fourier conduit donc à des positions atomiques situées à des distances $2\epsilon_i$ des positions

correctes, ϵ_i étant l'erreur dans l'emplacement des atomes calculée sans tenir compte de l'incertitude des angles des phases.

Ceci confirme la conclusion de Cruickshank (1950), à savoir que, toutes choses égales d'ailleurs, les positions atomiques déterminées par la méthode des transformations de Fourier dans les structures non-centrosymétriques sont affectées par des erreurs deux fois plus grandes que celles obtenues dans les structures avec centre de symétrie.

Nous tenons à exprimer notre reconnaissance pour M. D. W. J. Cruickshank, dont les critiques nous ont aidé à donner à ce travail la forme définitive.

APPENDICE

M. le Professeur Mauguin a bien voulu me signaler une démonstration simple de la formule (3):

$$|F(\mathbf{s})| e^{i\alpha} = \sum_{\nu} f_{\nu} \exp [i2\pi(\mathbf{r}_{\nu} \times \mathbf{s})].$$

Donnons à l'atome n le déplacement Δr_n , il vient:

$$\begin{aligned} e^{i\alpha\Delta} |F(\mathbf{s})| + i |F(\mathbf{s})| e^{i\alpha\Delta} \\ = i2\pi(\Delta r_n \times \mathbf{s}) f_n \exp [i2\pi(\mathbf{r}_n \times \mathbf{s})], \\ \Delta |F(\mathbf{s})| + i |F(\mathbf{s})| \Delta\alpha \\ = i2\pi(\Delta r_n \times \mathbf{s}) f_n \exp [i\{2\pi(\mathbf{r}_n \times \mathbf{s}) - \alpha\}]. \end{aligned}$$

En égalant les coefficients de i dans les deux membres:

$$|F(\mathbf{s})| \Delta\alpha = 2\pi(\Delta r_n \times \mathbf{s}) f_n \cos [2\pi(\mathbf{r}_n \times \mathbf{s}) - \alpha].$$

Bibliographie

- BOOTH, A. D. (1946). *Trans. Faraday Soc.* **42**, 617.
CRUICKSHANK, D. W. J. (1950). *Acta Cryst.* **3**, 10.

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The Crystal Structure of 1, 2-Dichloroethane at -50°C .

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Crystals of 1, 2-dichloroethane, $\text{ClCH}_2\text{CH}_2\text{Cl}$, are monoclinic, space group $C_{2h}^5-P2_1/c$, with two molecules in a unit cell of dimensions $a = 5.04$, $b = 5.56$, $c = 8.00$ Å., and $\beta = 109\frac{1}{2}^{\circ}$. The chlorine atoms lie in the general positions with parameters $x = 0.303$, $y = 0.279$, $z = 0.074$. The molecule is in the extended configuration with a chlorine-chlorine distance of 4.24 Å., and has a center of symmetry. The CH_2 groups show nearly free rotation, or almost complete orientational disorder, approximately about the chlorine-chlorine axis.

Introduction

The heat-capacity curve of 1, 2-dichloroethane (Pitzer, 1940) shows a large peak indicating a transition near 177°K . A nuclear magnetic resonance study (Gutowsky & Pake, 1950) suggests that between the transition and

the melting-point the molecule is rotating about, approximately, the Cl...Cl axis, and that it shows no rotation about an axis perpendicular to the line joining the carbon atoms (presumably an axis perpendicular to the instantaneous plane of the molecule). This latter

conclusion is in agreement with the dielectric-constant data (White & Morgan, 1937). There have been several reports that 1,2-dichloroethane shows rotational isomerism in the vapor phase. Bernstein (1949) has reported that the ratio of the number of molecules with the 'gauche' form to the number with the *trans* form is 0.29 in the vapor phase at room temperature. Ehrhardt (1932) has reported on the basis of an X-ray diffraction analysis of the vapor that the compound exists entirely in the *trans* form with a chlorine-chlorine distance of 4.4 Å. There has been no report of the crystal structure of 1,2-dichloroethane. However, Klug (1935 *a, b*) reported the structure of 1,2-diiodoethane in which the iodine atoms were located. This molecule has the *trans* form in the solid state. On the basis of Raman-spectra studies, Mizushima and others (Mizushima, Morino & Noziri, 1936; Mizushima, Morino, Watanabé, Simanouti & Yamaguchi, 1948; Ichisima & Mizushima, 1950) reported that in the solid state of 1,2-dichloroethane all molecules have the *trans* configuration.

This investigation is part of a series of structure determinations from single crystals at low temperature. Its purpose is the investigation of the nature of the disorder in the high-temperature form of crystalline 1,2-dichloroethane. A study of the low-temperature form and of the nature of the transition is now in progress.

Experimental

The techniques of the low-temperature study are described elsewhere (Abrahams, Collin, Lipscomb & Reed, 1950). Zero- and first-level precession photographs were taken about [100]. Precession angles of 23° for the zero level and 20° for the first level were used. Oscillation and rotation photographs and zero-, first- and second-level Weissenberg photographs were taken about [010]. Mo $K\alpha$ radiation was used throughout. The multiple-film technique, in which the films were interleaved with 0.029 mm. brass foil, was used for the $0kl$, $h0l$, $h1l$ and $h2l$ photographs.

The unit cell and space group were determined from the photographs in the usual manner. The intensities of the $h0l$, $h1l$, $h2l$ and $0kl$ reflections were estimated visually by comparison with a standard scale. The values for the magnitudes of the structure factors were derived from the intensities in the usual way, and are collected in Table 1 under F_o .

A minimum value of the density of the solid compound was determined by measuring the contraction in volume on freezing the liquid, whose density was known.

Crystal data

The compound 1,2-dichloroethane, $\text{ClCH}_2\text{CH}_2\text{Cl}$, has a molecular weight of 98.97 and a melting-point of -35.3°C . The crystals are monoclinic with

$$a = 5.04 \pm 0.02, \quad b = 5.56 \pm 0.02, \quad c = 8.00 \pm 0.02 \text{ Å.},$$

and

$$\beta = 109\frac{1}{2}^{\circ} \pm \frac{1}{2}^{\circ},$$

and with two molecules in the unit cell. The observed density is not less than 1.47 g.cm.^{-3} , while the calculated density is 1.55 g.cm.^{-3} . The only systematic extinctions observed were $0k0$ with k odd and $h0l$ with l odd. These are consistent with the space group $C_{2h}^5-P2_1/c$.

Analysis and discussion of structure

The unit cell contains four chlorine atoms which were placed in the general positions listed in the *Internationale Tabellen* (1935) as

$$4(e) \quad x, y, z; \quad \bar{x}, \bar{y}, \bar{z}; \quad \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z; \quad x, \frac{1}{2} - y, \frac{1}{2} + z.$$

The Patterson function $p(x, z)$ was evaluated and gave well-resolved peaks at $x=0.60$, $z=0.16$ and the equivalent positions. These peaks were attributed to vectors between equivalent chlorine atoms. The ambiguity in the chlorine positions of $p(x, z)$ was resolved by placing the center of the molecule at a symmetry center rather than on a twofold screw axis. Approximate x and z chlorine parameters derived from $p(x, z)$ were

$$x_{\text{Cl}} = 0.300, \quad z_{\text{Cl}} = 0.075.$$

Since the molecule contains only chlorine, carbon and hydrogen, in our initial calculations we assumed that the signs of the F_{h0l} and F_{0kl} could be determined by the contribution of chlorine alone. Using the approximate x and z parameters for chlorine obtained from $p(x, z)$, the Fourier projection $\rho(x, z)$ was evaluated (Fig. 1). An approximate y parameter for chlorine was computed from the x and z parameters of $\rho(x, z)$ and a chlorine-chlorine distance of 4.3 Å., corresponding to the *trans* configuration. The Fourier projection $\rho(y, z)$ was then evaluated.

From the new chlorine parameters of $\rho(y, z)$ and $\rho(x, z)$, structure factors were then calculated including the carbon contribution. The molecular model was $\text{Cl}\dots\text{Cl} = 4.24$, $\text{C}-\text{Cl} = 1.74$ and $\text{C}-\text{C} = 1.45$ Å. With the assumption, suggested by the projections, of free rotation about the $\text{Cl}\dots\text{Cl}$ axis, the expression for the structure factor became

$$k+l \text{ even: } F_{hkl} = 4f_{\text{Cl}} \cos 2\pi(hx_{\text{Cl}} + lz_{\text{Cl}}) \cos 2\pi ky_{\text{Cl}} \\ + 4f_{\text{C}} J_0(2\pi\rho | \mathbf{h} | \sin \psi) \cos 2\pi(hx_{\text{OC}} + lz_{\text{OC}}) \cos 2\pi ky_{\text{OC}},$$

$$k+l \text{ odd: } F_{hkl} = -4f_{\text{Cl}} \sin 2\pi(hx_{\text{Cl}} + lz_{\text{Cl}}) \sin 2\pi ky_{\text{Cl}} \\ - 4f_{\text{C}} J_0(2\pi\rho | \mathbf{h} | \sin \psi) \sin 2\pi(hx_{\text{OC}} + lz_{\text{OC}}) \sin 2\pi ky_{\text{OC}},$$

where f_{Cl} and f_{C} are the atomic scattering factors for chlorine and carbon, respectively; x_{Cl} , y_{Cl} , z_{Cl} are the chlorine parameters; x_{OC} , y_{OC} , z_{OC} are co-ordinates of the center of rotation of the carbon atom; J_0 is the zero-order Bessel function; ρ is the radius of rotation of the carbon atom; \mathbf{h} is the reciprocal-lattice vector; and ψ is the angle between the axis of rotation and the vector \mathbf{h} . The scattering curves were taken from the *Internationale Tabellen* (1935) after multiplication by the temperature factor $\exp[-B(\sin \theta/\lambda)^2]$ with $B=5.4$.

Computation of the structure factors showed that none of the F_{h0l} changed sign, but that one of the F_{0kl}

Table 1. *Observed and calculated structure factors*

<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c
002	37.4	+39.8	112	10.0	-11.1	125	<4.5	+4.2
004	10.0	-6.6	113	6.0	+7.1	124	17.6	-19.3
006	12.5	-13.1	114	13.9	+11.4	125	<5.9	-2.5
008	5.5	-5.4	115	<7.4	+1.3	126	6.8	-7.4
100	<3.6	-4.3	116	7.9	+9.7	220	20.3	+21.0
102	30.3	-29.8	111	15.9	+10.1	221	6.8	-10.0
104	18.7	-16.0	112	33.9	-34.9	222	<5.4	+0.3
106	<2.8	0.0	113	<5.5	0.0	223	6.3	-6.0
108	<3.2	+3.8	114	<6.0	-0.6	224	10.4	-8.8
102	39.4	+37.2	115	<6.4	-2.6	221	<4.5	-4.8
104	25.1	+32.0	116	8.4	+11.4	222	26.2	+25.4
106	6.2	+9.2	210	24.8	+15.6	223	5.9	+4.2
108	1.4	-2.5	211	8.4	+4.9	224	7.3	+7.5
200	24.0	-22.2	212	24.8	+20.8	225	<5.9	+4.6
202	<2.2	+2.5	213	<6.9	-0.9	226	6.8	-6.3
204	12.5	+12.0	214	9.4	+6.9	320	14.9	-12.6
206	3.9	+6.4	215	<7.9	-1.7	321	<6.3	-2.3
208	<3.2	+1.0	211	15.4	+10.7	322	15.8	-9.7
202	27.8	-28.2	212	10.9	-8.1	323	<7.2	+1.8
204	7.5	-7.2	213	<5.5	+6.9	324	<7.7	-1.6
206	5.5	+8.2	214	22.3	-21.9	321	8.6	-7.8
208	2.2	+6.8	215	<6.4	-0.1	322	<5.9	-0.3
300	20.8	+18.5	216	8.9	-11.7	323	<5.9	-6.5
302	16.2	+14.0	310	13.9	+8.9	324	9.0	+11.3
304	3.6	+2.0	311	<6.9	-2.7	325	<6.8	-1.2
306	<3.4	-2.5	312	7.4	-6.0	420	<7.2	-2.1
302	<2.2	+3.4	313	<7.9	-1.3	421	<7.7	+2.0
304	11.4	-14.3	314	8.4	-7.8	422	<8.2	+3.9
306	8.4	-10.0	311	<6.4	-0.7	421	<7.2	+1.7
308	1.4	-3.0	312	22.3	+20.0	422	10.3	-9.4
400	<2.6	+2.5	313	<6.4	+2.6	423	<7.2	+1.7
402	6.8	-5.6	314	10.0	+10.7	031	15.6	+12.7
404	4.3	-4.3	410	12.9	-11.3	032	17.8	+15.1
402	13.9	+12.2	411	<7.9	+0.2	033	2.6	+2.4
404	9.6	+10.7	412	<8.4	-6.0	034	12.2	+12.2
406	2.5	+0.6	411	<7.4	-1.5	035	4.0	-4.0
408	<3.2	-4.2	412	<7.4	-5.6	037	2.2	-3.0
500	6.8	-6.3	020	34.7	-31.0	040	14.9	+12.9
502	<3.4	-1.7	021	7.7	+5.2	041	5.5	-4.9
502	5.7	-5.1	022	14.9	-13.4	042	6.8	+6.7
504	<3.0	+1.4	023	10.9	+9.1	043	8.0	-8.5
506	1.6	+5.0	024	6.3	+7.1	044	3.9	-2.4
011	9.6	+5.2	025	5.9	+3.8	045	4.2	-3.6
012	32.6	-35.6	026	7.3	+9.9	046	3.7	-4.3
013	<2.2	3.9	120	18.5	+16.4	051	8.1	-7.1
014	21.8	-22.6	121	12.7	+4.7	052	5.5	-4.9
015	<2.7	2.4	122	27.1	+26.8	053	<2.7	-1.0
016	<2.8	-3.5	123	<5.4	-3.0	054	3.4	-4.0
017	<2.8	+1.3	124	12.2	+13.3	055	1.1	+2.9
018	2.2	+3.5	125	<7.2	-4.9	060	1.6	-2.8
110	49.6	-46.5	121	12.2	+10.1			
111	17.9	+14.1	122	14.0	-12.5			

did. The function $\rho(y, z)$ was then re-evaluated and the structure factors were computed again; no further sign changes occurred. The Fourier series were evaluated at intervals of 6° along a and b , and careful sections were drawn before plotting the electron-density maps.

The final values of the calculated structure factors are listed in Table 1 under F_c , and the final Fourier projections $\rho(x, z)$ and $\rho(y, z)$ are shown in Figs. 1 and 3, respectively. The interpretations of these projections are shown in Figs. 2 and 4. Although for convenience in the calculations we assumed that the molecule was rotating about the chlorine-chlorine axis, it is more probable that it is rotating about the least moment of inertia, as is suggested by the slightly unsymmetrical nature of the chlorine peaks in both projections. It seems possible also from the two projections that the

disorder of the CH_2 group is not really complete but favors slightly the carbon position at $x_C=0.13, y_C=0.04, z_C=0.065$. Inasmuch as placement of the carbon atom in this position made no change in either projection, it may be concluded that whether or not the disorder is complete, it is certainly real. This conclusion is strongly supported by the fact that the electron densities symmetrically disposed on the other side of the Cl...Cl axis from the apparent maximum is about 3.6 e.A.^{-2} in both $\rho(x, z)$ and $\rho(y, z)$ as compared with the density of about 4.4 e.A.^{-2} at the apparent maximum. Thus within the limits of errors of our electron-density projections the disorder appears to be complete, but there does also exist the possibility that the difference indicated here is real and that at -50° C. a transition to a partially ordered structure has begun. In any case the con-

figuration and nature of the disorder as suggested by the Raman and nuclear magnetic resonance studies has proved to be essentially correct.

The possibility of incipient phase transition at -50°C . appears to be confirmed by preliminary

are the calculated values for the ordered structure, $F_{006} = 18.6$, $F_{102} = 38.8$, $F_{206} = 10.3$, and $F_{20\bar{4}} = 3.7$. It is felt that any other ordered structure would produce similar disagreement with the F_o of Table 1, and therefore that the disorder is confirmed.

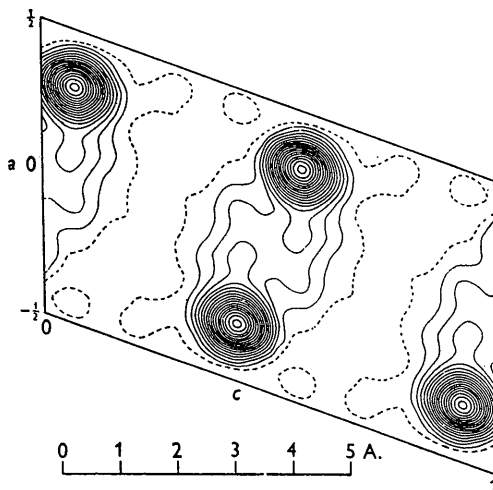


Fig. 1. Projection of electron density along [010]. Contours are in e.A.^{-2} , the one-electron contour being broken. The complete unit cell is shown.

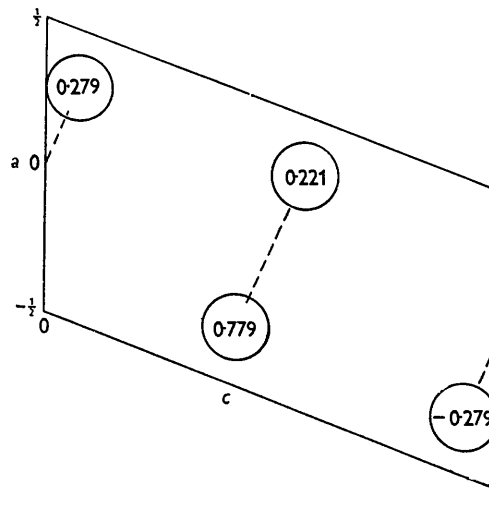


Fig. 2. Line diagram of Fig. 1, showing out-of-plane co-ordinates of the chlorine atoms.

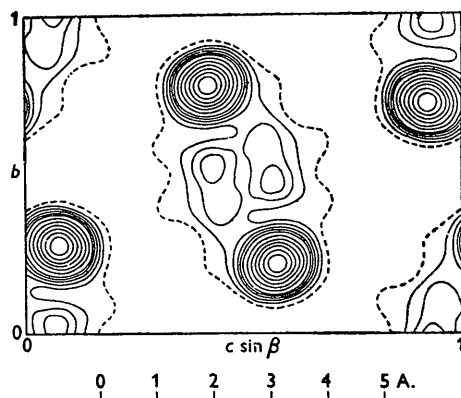


Fig. 3. Projection of electron density along [100]. Contours are in e.A.^{-2} . The one-electron contour is broken, and odd-numbered contours from 7 through 19 have been omitted. The complete unit cell is shown.

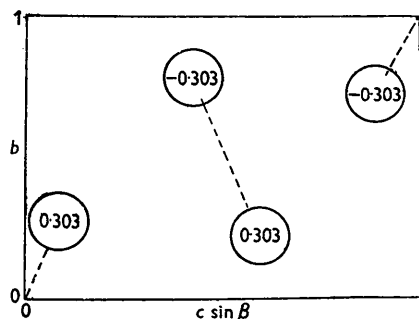


Fig. 4. Line diagram of Fig. 3, showing out-of-plane co-ordinates of the chlorine atoms.

Fourier results obtained by Mr T. B. Reed on the low-temperature form. This form is isomorphous with the -50°C . form but with ordered and well-resolved carbon atoms for which preliminary x and z parameters are 0.11 and 0.09, respectively. Calculation of F_{h0l} with these parameters and with the chlorine positions $x = 0.303$ and $z = 0.074$ gave significantly poorer agreement with F_o than did the F_c in Table 1. Only the unobserved F_{202} changed sign. This ordered structure gave a discrepancy ($\sum ||F_o| - |F_c|| \div \sum |F_o|$ using only observed data) of 21% as compared with 15% for the disordered structure, and gave a sum of squares of residuals over twice as great as that for the disordered structure of Table 1. Specific examples of disagreement

The final chlorine parameters, as determined from $\rho(x, z)$ and $\rho(y, z)$, are $x_{\text{Cl}} = 0.303$, $y_{\text{Cl}} = 0.279$, $z_{\text{Cl}} = 0.074$. Estimated probable errors are 0.002, 0.004 and 0.002, respectively.

The shortest chlorine-chlorine intermolecular distances are 4.01 Å. (approximately along c) and 3.79 Å., somewhat greater than 3.6 Å., which is twice the van der Waals radius of chlorine. Although exact bond lengths would be of interest in 1, 2-dichloroethane, no attempt was made in the present study to determine them, since it is clear from preliminary results on the low-temperature form that the resolution in the Fourier projections will be much better than in those given here. It is of interest that the molecule is in the extended

configuration, and that the intramolecular chlorine-chlorine distance is 4.24 ± 0.04 Å.

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References

- ABRAHAMS, S. C., COLLIN, R. I., LIPSCOMB, W. N. & REED, T. B. (1950). *Rev. Sci. Instrum.* **21**, 396.
 BERNSTEIN, H. J. (1949). *J. Chem. Phys.* **17**, 258.
 EHRHARDT, F. (1932). *Phys. Z.* **33**, 605.

- GUTOWSKY, H. S. & PAKE, G. E. (1950). *J. Chem. Phys.* **18**, 162.
 ICHISIMA, I. & MIZUSHIMA, S. (1950). *J. Chem. Phys.* **18**, 1420.
Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Berlin: Borntraeger.
 KLUG, H. P. (1935a). *Z. Krystallogr.* **90**, 495.
 KLUG, H. P. (1935b). *J. Chem. Phys.* **3**, 747.
 MIZUSHIMA, S., MORINO, Y. & NOZIRI, S. (1936). *Nature, Lond.*, **137**, 945.
 MIZUSHIMA, S., MORINO, Y., WATANABÉ, I., SIMANOUTI, T. & YAMAGUCHI, S. (1948). *J. Chem. Phys.* **17**, 591.
 PITZER, K. S. (1940). *J. Amer. Chem. Soc.* **62**, 331.
 WHITE, A. H. & MORGAN, S. O. (1937). *J. Chem. Phys.* **5**, 655.

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A Study of the Unit-cell Dimensions and Symmetry of certain Ferroelectric Compounds of Niobium and Tantalum at Room Temperature

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An account is given of the methods of preparation of the recently reported ferroelectric compounds KTaO_3 , KNbO_3 , NaNbO_3 and NaTaO_3 , and of an investigation of their structure from powder photographs. At room temperature KTaO_3 is cubic and the other compounds orthorhombic, the distortion from the simple perovskite structure being similar to that which BaTiO_3 shows between -5 and 90° C. From an examination of the variation of Curie point with lattice parameter of these compounds, it is suggested that the factor primarily responsible for the ferroelectricity is the degree of homopolar bonding of the tantalum, niobium or titanium ion with the oxygen ion.

Introduction

In a recent note Matthias (1949) reported that the niobates and tantalates of sodium and potassium, which are pseudo-isomorphous with BaTiO_3 , exhibit ferroelectric properties. These salts gave a piezoelectric response and showed dielectric hysteresis loops, with peaks in their dielectric constant versus temperature curve corresponding to changes in crystal symmetry. These changes in symmetry were observed by studying crystals, of 1–2 mm. cube edge, with the polarizing microscope. The room-temperature symmetry of the compounds was given as pseudo-tetragonal from a study of the X-ray powder photographs, with an axial ratio of ≈ 0.99 for the niobates, and rather closer to unity for the tantalates. The observations described below, which have been previously briefly reported (Vousden, 1951), were undertaken in order to make accurate determinations of the unit-cell dimensions of these compounds.

Crystallization of the substances

The compounds were produced as small crystals, of volume of the order of 10^{-10} cm.³, from the oxides of

tantalum and niobium, of purity 99 and 99.7 % respectively. No chemical analysis of the products was undertaken, but the constancy of the parameters of the same materials prepared under different conditions, or in some cases by different methods, suggested that the effect of any impurity content was negligible.

NaNbO_3

A suspension of Nb_2O_5 in NaOH was boiled for about 20 min., and the precipitate, consisting of very small crystals of linear dimensions less than 10^{-4} cm., was filtered and then dried at about 400° C. The powder photograph of the product showed the symmetry of the structure to be cubic, but the line broadening showed the existence of considerable lattice strain. Annealing the compound at about 1100° C. improved the diffraction pattern so that the groups of lines corresponding to the pseudocubic distortion were clearly resolved.

KNbO_3

Equimolecular proportions of KOH and Nb_2O_5 were fused at 400° C. in a platinum crucible. The resulting product, consisting of a white crystalline powder, was then reground and reheated to the same temperature several times in order that the reaction might be more

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