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The crystal structure of the high temperature form of choline chloride.* By PAUL SHANLEY and ROBERT L. COLLIN, *Cancer Research Institute, New England Deaconess Hospital, Boston 15, Massachusetts, U.S.A.*

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Choline chloride, $(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}^+\text{Cl}^-$, is extremely sensitive to ionizing radiation in the solid state at room temperature (Tolbert *et al.*, 1953; Lemmon *et al.*, 1955, 1958). Around 80 °C. the orthorhombic form (Senko & Templeton, 1960) transforms to a cubic form (Collin, 1957) which is stable to ionizing radiation (Serlin, 1957 and unpublished work of the authors). We wish to report here an extension of the X-ray studies on the high temperature form.

The original X-ray study (Collin, 1957) showed the crystals at 85 °C. to be face-centered cubic with axial length 9.48 ± 0.03 Å. A combination of the density reported by Senko & Templeton (1960) at 20 °C. and our unpublished thermal expansion measurements between 20 and 85 °C. gave a density of 1.12 g.cm.⁻³ at 85 °C. This requires 4 molecules per unit cell (calculated density is 1.09 g.cm.⁻³).

Intensities were estimated on powder and single crystal precession photographs taken at 85 °C. Single crystals of the high temperature phase were formed by heating a single crystal in a stream of hot air slowly through the transition region. The crystal transformed essentially as a single crystal but there were always a few satellite spots from small amounts of randomly oriented crystals. In addition, intensity estimates of the eight strongest lines were made on powder samples pressed into a flat cake in a lucite frame and mounted on a proportional counter spectrogoniometer. The sample cake had a thermocouple embedded in it and was maintained at 85 °C. by irradiating the front face with a 250 watt infrared lamp. The intensities measured in this way were in good agreement with those measured by photographic means but

Table 1. Comparison of observed and calculated structure factors for a model with a spherically disordered choline ion

<i>hkl</i>	F_c	$ F_o $	<i>hkl</i>	F_c	$ F_o $
111	-5	14	331	-13	10
200	77	74	420	14	13
220	36	40	422	10	10
311	-25	22	511	-7	11
222	24	28	333	-7	7
400	18	2	440	6	9

where reflections had been measured by both methods the spectrogoniometer values were preferred. The observed structure amplitudes, corrected by Lorentz, polarization and multiplicity factors, are given in Table 1 as F_o .

Since a choline ion can have at most a mirror plane, the face-centered cubic structure with 4 molecules per unit cell must be disordered. An attempt was first made to see whether this disordering was spherical by calculating structure factors for a room temperature choline ion spherically disordered about its center of mass (Zachariasen, 1945). An overall temperature factor of 22 Å was used to get the best agreement between observed and calculated values. The results are shown in Table 1 under F_c . If the (111) and (400) reflections are ignored, the agreement is good, and one would suspect that the disorder of the choline ion cannot be too far from spherical. However, the poor agreement for the (111) and (400) reflections rules out a strictly spherical disorder.

Further progress in elucidating the structure of the high temperature form does not appear possible without assumptions which, although physically reasonable, cannot be rigorously proved. The first assumption is that the disordered structure is centrosymmetric, and the second is that, in view of the good agreement for most of the reflections in Table 1, the signs of the reflections are correctly determined by the spherically disordered model, with the possible exception of (111) and (400).

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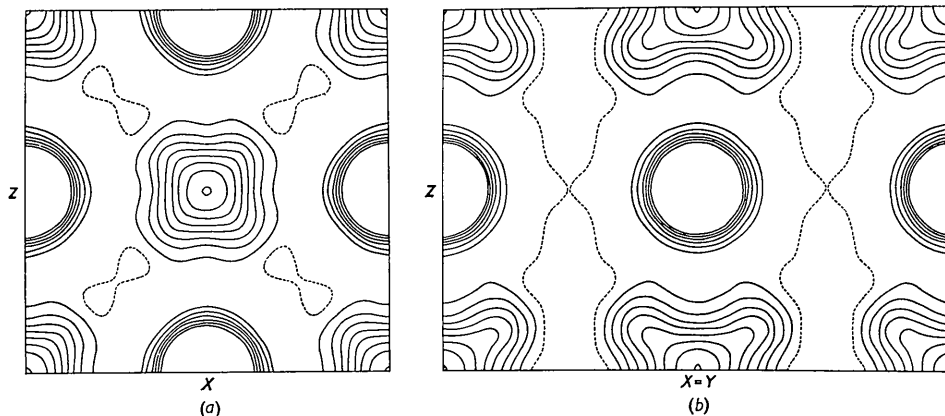


Fig. 1. Electron-density sections. (a) $y=0$ and (b) $x=y$. The contour interval is 0.1 e.Å^{-3} . The 0.2 e.Å^{-3} contour is dashed and the contours above 0.8 e.Å^{-3} around the chloride ion have been omitted.

With these assumptions three-dimensional electron-density calculations were made using signs, for all but the (400) and (111) reflections, obtained from the spherically disordered model. The (400) reflection was put into the calculation as zero since its observed structure amplitude is small and its sign unknown. The sign of the (111) reflection was taken positive in one calculation and negative in the other. The Fourier expression was evaluated over the asymmetric unit at intervals of 1/40 of the unit-cell edge. For both (111) sign choices the choline ion appeared more extended in the body diagonal direction than in any other. A distortion of the spherical choline model in this way would decrease the contribution of the choline to the (111) structure factor and hence the sign of this reflection would be the same as that of the chloride contribution, negative. Electron-density maps of the $y=0$ and $x=y$ sections with the sign of $F(111)$ negative are shown in Fig. 1. Calculations with the chloride ion contribution subtracted out show little change in the contours around the choline ion, and hence the observed asymmetry of this ion cannot be attributed to diffraction effects from the much heavier chloride ion.

That the choline ions tend to lie along the body diagonals is not surprising since this is the direction in which most room exists, 16.4 Å between the two neighboring chloride ions. It is not possible to say whether the

disorder is static or whether the choline ion is a hindered rotator in an octahedral potential field. No prominent diffuse scattering has been observed in the high temperature phase.

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A neutron diffraction study of orthorhombic PbO.* MORTIMER I. KAY,† *Brookhaven National Laboratory, Upton, New York, U.S.A. and Crystal Research Laboratory, Department of Physics, The Pennsylvania State University, University Park, Pa., U.S.A.*

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The structure of tetragonal (red) PbO (Moore & Pauling, 1941) is comprised of layers of oxygen sandwiched between layers of lead, the lead being at the apex of a PbO₄ pyramid with a square O₄ base. The Pb-O-Pb layers repeat in c .

Bystrom (1943) attempted to determine the structure of orthorhombic (yellow) PbO. He placed the Pb atoms quite well, but could only surmise the oxygen coordinates. He reported the space group to be either $Pbma$ or $Pb2a$, $N=4$. The leads or oxygens by themselves must be in the centrosymmetric $Pbma$; however, unless both atoms have the same y coordinates, the space group must be the non-centrosymmetric $Pb2a$. It was this that Bystrom felt contained his most 'logical' structure.

Since tetragonal PbO shows an interesting chemical bonding scheme, and since the oxygen in the yellow (orthorhombic) phase could not be found by means of X-ray data, a neutron powder diffraction pattern of the latter was taken.

The unit-cell edges used were those determined at the

National Bureau of Standards (Swanson & Fuyat, 1953). They are

$$a = 5.489, b = 4.775, c = 5.891 \text{ \AA}.$$

Simultaneous equations utilizing the $h0l$ data readily established the x and z coordinates, which would be the same in either space group. The y parameter for Pb was taken as 0.25. The remaining O coordinate (y) was then found from hkl data to be equal or very close to the 0.25 assigned to Pb. $Pbma$ was thus accepted as the probable space group. The positions are: $x, \frac{1}{4}, z$; $\bar{x}, \frac{3}{4}, \bar{z}$; $\frac{1}{2} + x, \frac{1}{4}, \bar{z}$; $\frac{1}{2} - x, \frac{3}{4}, z$.

Final refinement was carried out on the x and z coordinates using Busing & Levy's (1958) least-squares program with the measurable single reflections. A few preliminary rounds of refinement showed that the structure factors included did not go far enough out in reciprocal space to give meaningful temperature factors. Therefore, B was assumed to be 0.8 Å² for lead and 1.2 Å² for oxygen, on the basis of similar structures. The final $R' = \Sigma |F_o^2 - F_c^2| / \Sigma F_o^2$ for the included reflections was 0.04. When all intensities were included, $\Sigma |I_o - I_c| / \Sigma I_o$ rose to 0.071. Refinement was thus considered satisfactory. The observed and calculated intensities are given in Table 1. The final parameters are given in Table 2, together with Bystrom's results.

It is seen from Fig. 1 that the Pb-O-Pb layers are

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