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The Structure of Caesium Nitrate

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STARTING with some investigations on the rotation of anions in cubic crystals we had the opportunity of studying the crystal structure of a series of nitrates including CsNO_3 in the temperature interval between room temperature and the melting point. The results of these investigations have been or will be published elsewhere, but a brief account on the caesium nitrate work is given in the present article because our results contradict those published in this journal by L. Waldbauer and D. C. McCann.¹

Beside the x-ray investigation, an optical examination of the crystals in polarized light was carried out, and the correctness of the result of Gossner² and also Wallerant³ definitely confirmed, CsNO_3 indeed being cubic between the transition point at 161° and the melting point. X-ray data of the cubic form of CsNO_3 have recently been published by the present authors in a paper dealing with cubic nitrates of monovalent cations.⁴

Single crystals of CsNO_3 are not destroyed when heated above the transition temperature (to 200°C) and then cooled down to room temperature. Rotation photographs of the same crystal taken (a) at room temperature (b) at 200°C and (c) after cooling back to room temperature are shown in Fig. 1.⁵ From the reversible character of the transition of single crystals and the fact that diffraction patterns at ordinary temperature and at 200° are nearly identical (except for the weakening of the reflections at greater angles at 200°) the conclusion must be drawn that the positions of the Cs^+ ions are very

little altered during the process of transition. The Cs^+ ion lattice in the high temperature form is a simple cubic one with a lattice constant of about 4.49Å, and so we must assume it to be a pseudocubic lattice with $\sim 4.45\text{Å}$ in the low temperature form.

It seems extremely difficult to determine the true symmetry of the caesium nitrate crystals in the low temperature form. Apparently no reliable observations exist indicating a biaxial character of the crystals, but the close resemblance with rubidium nitrate crystals which are no doubt orthorhombic makes the assumption of hexagonal symmetry rather problematic. If this assumption is made, however, we are able to show that the most probable space group is C_{3v}^2 . The only possible coordinates for the caesium ions having hexagonal symmetry and leading to the pseudocubic arrangement mentioned above are:

$$\begin{array}{ccccccc} 0 & 0 & 0 & \frac{1}{3} & \frac{2}{3} & 0 & \frac{2}{3} & \frac{1}{3} & 0 & x & 0 & z & 0 & x & z & \bar{x} & 0 & \bar{z} \\ & & & & & & & & & 0 & \bar{x} & \bar{z} & x & x & \bar{z} & \text{and} & \bar{x} & \bar{x} & z \end{array}$$

x being nearly $\frac{1}{3}$ and z nearly $\frac{2}{3}$. Possible space groups are: C_3^1 , C_{3i}^1 , C_{3v}^2 , D_3^1 and D_{3d}^1 . The crystal classes C_{3i} and D_{3d} possessing both a center of symmetry must be rejected, however, because CsNO_3 crystals according to our observations are strongly pyroelectric (the same result was obtained with RbNO_3 crystals). A considerable number of CsNO_3 crystals was examined under the microscope, the development of crystal faces indicating that the class D_3 has to be excluded also. The distinction between the two remaining classes C_3 and C_{3v} is not so easily performed, but it seems at least very probable that under the condition in question the trigonal-pyramidal class is the right one and the space group of CsNO_3 C_{3v}^2 . It is interesting to notice that our result referring to caesium nitrate is just the result to which Pauling and Sherman were led, though in a somewhat different way, in the case of rubidium nitrate.⁶

¹ L. Waldbauer and D. C. McCann, *J. Chem. Phys.* **2**, 615 (1934).

² Gossner, *Zeits. f. Krist.* **38**, 144 (1904).

³ Wallerant, *Bull. Soc. fr. min.* **28**, 325 (1905).

⁴ C. Finbak and O. Hassel, *Zeits. f. physik. Chemie* **B35**, 25 (1937).

⁵ The photographs reproduced here are taken with Cu-radiation. Close to the incident beam, layer-lines due to the secondary emitted Cs K radiation may be observed. See Finbak and Hassel, *Norsk. geol. Tidsskr.* **16** (1936), *Nature* **139**, 194 (1937), *Avh. Oet. Norske Vid. Akad. Oslo I Mat-natv. Kl.* (1937) No. 2.

⁶ Pauling and Sherman, *Zeits. f. Krist.* **84**, 213 (1933).

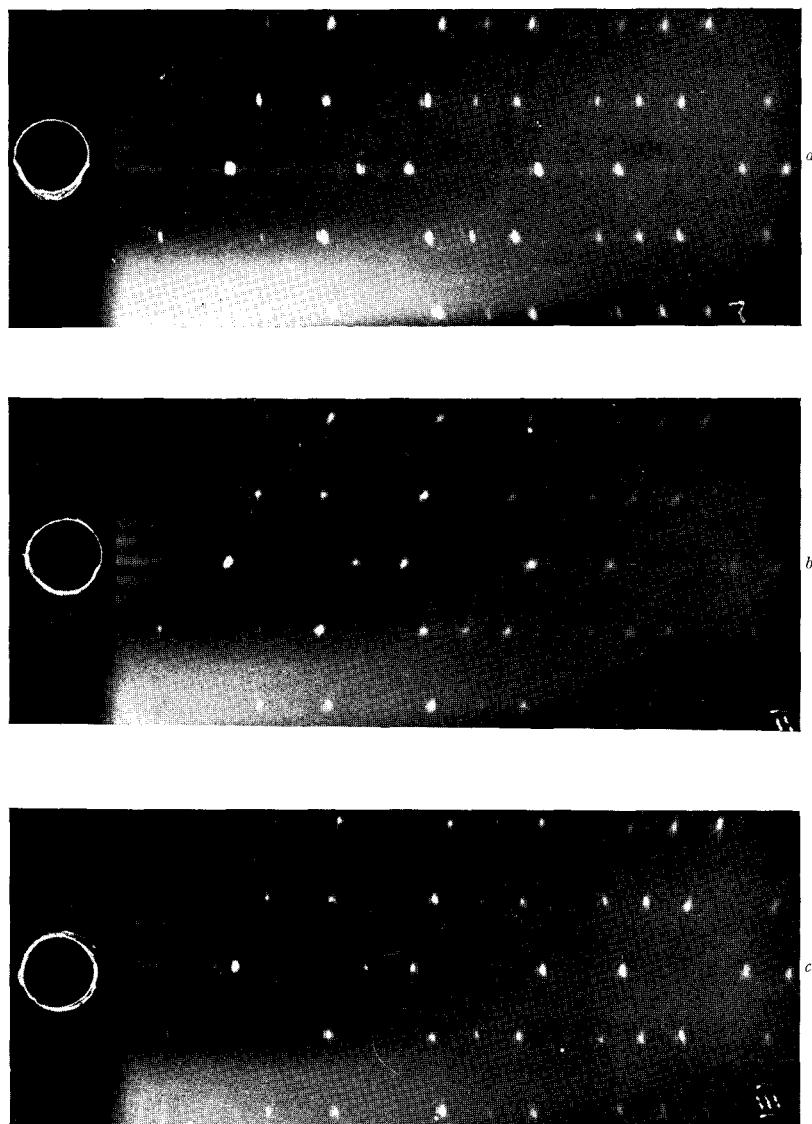


FIG. 1.



FIG. 2.

Fig. 2 shows part of a rotation photograph of CsNO_3 , the orthohexagonal a axis being the axis of rotation. The weaker layer-lines indicate that the true period in the direction of this axis is not given by the period of the Cs^+ but is three times as large. In the paper of Waldbauer and McCann are to be found reproductions of powder photographs of CsCl , CsI , KIO_3 and CsNO_3 . The apparently very high degree of resemblance between the photograph of CsI and CsNO_3 is rather misleading, however.