

Caesium Nitrate and the Perovskite Structure

Louis Waldbauer and D. C. McCann

Citation: [The Journal of Chemical Physics](#) **2**, 615 (1934); doi: 10.1063/1.1749542

View online: <http://dx.doi.org/10.1063/1.1749542>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/2/9?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Simultaneous Stark and Zeeman effects in atoms with hyperfine structure](#)

Am. J. Phys. **81**, 936 (2013); 10.1119/1.4823999

[Modification of the electronic structure in a carbon nanotube with the charge dopant encapsulation](#)

Appl. Phys. Lett. **92**, 193110 (2008); 10.1063/1.2929381

[Plasma structure and behavior in a disk magnetohydrodynamic generator](#)

J. Appl. Phys. **96**, 5441 (2004); 10.1063/1.1803929

[Single ion mass spectrometry and the fine structure constant](#)

AIP Conf. Proc. **551**, 73 (2001); 10.1063/1.1354340

[Scaling properties of the \$\nu_1\$ Raman active nitrate mode in doped ammonium and potassium nitrate crystals](#)

J. Chem. Phys. **109**, 10311 (1998); 10.1063/1.477726



maximum. The field in question should be of the order 70 kv/cm for transformer oil, and 200 kv/cm for glass.

The data given by Toriyama²⁹ for the conductance of transformer oil indicate that the saturation current may indeed increase very rapidly with the field intensity. The effects found by Toriyama were somewhat larger than could be accounted for by the theory (assuming univalent ions); the cause of the discrepancy would have to be determined before definite conclusions could be drawn.

Where the saturation current is found to increase with the field intensity, it should be possible to find evidence of the Langevin time-lags. Where the saturation current is independent of the field intensity, the distribution of space charges ought to correspond to a greater, chemical time-lag.

In a given experiment, some electrolytes may show a Langevin time-lag, others a chemical

time-lag. Whether a given electrolyte will show one or the other, will depend on two properties that cannot in general be predicted, namely, the ratio τ_c/τ_L and the reserve concentration of ion pairs. Incidentally, the pair concentration and τ_L will depend on the concentration of ions, the latter inversely as the conductance. The chemical time-lag ought not to depend on the concentration unless the electrolyte is polymerized, or cluster ions are formed. It must be pointed out, however, that cluster ions may form at surprisingly low concentrations.¹¹

As yet, time-lags or saturation currents have not been measured for electrolytes of known constitution in solvents of low dielectric constants. By such methods, it should be possible to determine the mobilities of suitable free ions in benzene and similar solvents, where there is no hope that we should ever be able to extrapolate conductance curves. Moreover, the investigation of these phenomena in known electrolytes would greatly aid their application to the study of semiconductors of unknown constitution.

²⁹ Y. Toriyama, *Archiv f. Electrotech.* **19**, 31 (1927).

Caesium Nitrate and the Perovskite Structure

LOUIS WALDBAUER AND D. C. McCANN, *Division of Analytical Chemistry, State University of Iowa*

(Received June 15, 1934)

1. The crystal structure of dysanlyte has been verified. 2. The crystal structure of CsNO_3 has been determined. 3. The so-called perovskite structure as a type of cubic symmetry is based on a mineral which is very probably not cubic but is orthorhombic. 4. The term "perovskite structure" should be discontinued.

THE authors' interest was first directed to the perovskite structure when a powder diffraction pattern of CsNO_3 was found to suggest cubic symmetry (Fig. 1) while the weak birefringence, as shown by the polarizing microscope, indicated some other symmetry.

Wyckoff¹ discussed the assignment of crystals, giving a pattern of this kind, to the so-called perovskite structure and expressed his doubt that these crystals were really isometric. Barth² made the first structure determination of pe-

rovskite and reported the mineral to be orthorhombic, $a : b : c = 0.9881 : 1 : 1.4078$, and the space group to be V_h ¹⁹. Barth² also determined the structure of dysanlyte to be cubic with $a_0 = 3.826$. The authors of this paper were able to check Barth's work on dysanlyte, using a sample from Magnet Cave, Arkansas (see Table I).

The authors were unable to obtain a sample of perovskite but, in view of Table I, saw no reason to doubt Barth's work. It therefore seemed worthwhile to make a complete structure analysis of CsNO_3 , since the "perovskite structure" was in question and the structure of CsNO_3 had never been determined.

¹ R. W. G. Wyckoff, *Structure of Crystals*, Chemical Catalogue Company, New York, 1931.

² T. Barth, *Norsk. Geology Tidsskr.* **8**, 201 (1925).

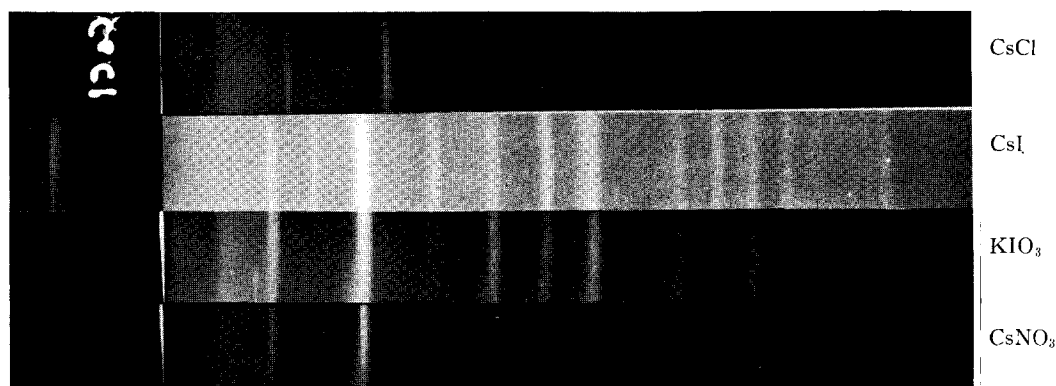


FIG. 1.

TABLE I. *Dysanalyte.*

	Barth	Waldbauer and McCann
Symmetry	cubic	cubic
Space group	O_h^1 , O^1 or T_d^1	O_h^1 , O or T_d^1
a_0	3.826	3.80

The usual methods of crystal analysis were used. Several Laue photographs were obtained, all of which indicated hexagonal symmetry. Oscillation photographs were used for measurement of spacings along the axes. A gnomonic projection (Fig. 2) of a Laue photograph of CsNO_3 , with the x-ray parallel to the C axis, was made and indexed. From the indexed projection and the spacing measurements, values of $n\lambda$ were calculated and compared with the minimum possible wave-length. Wyckoff's statistical method and tables³ were used to determine the space group. The results are given in Table II.

TABLE II. *Symmetry data on CsNO_3 .*

a_0	10.74 Å
c_0	7.68 Å
mols per unit cell	9
Space lattice	Γ_h
Space groups (possible)	D_{3h}^1 , D_{3h}^3 , D_{3h}^4

The problem of the supposed inversion of CsNO_3 at 161° ⁴ was attacked by means of a heated camera built by the authors (Fig. 3). Powder diffraction photographs were obtained

at temperatures of 165° and 200° . These showed a pattern exactly comparable to those at room temperature except for a very slight shift due to expansion. The inference was, therefore, that no structure change took place. In view of the determination of RbNO_3 ⁵ a question arose, however. Rubidium nitrate was discussed both for the hexagonal and the orthorhombic symmetry, the conclusion being that it was very nearly hexagonal but actually orthorhombic. The decision seemed to be based on a biaxial interference figure. Caesium nitrate could be assigned to the orthorhombic axes with $a : b : c = 18.60 : 10.74 : 7.68$, a unit cell containing 18 mols. However, since CsNO_3 shows no biaxial interference figure and since the hexagonal cell is smaller, the orthorhombic assignment is not justified by any known data. The fact remains that CsNO_3 may be, through deviations within experimental error, orthorhombic at room temperature or above 161° .

A further discussion of Fig. 1 may be made. Caesium chloride and CsI are known to be cubic. Caesium nitrate has been shown to be hexagonal. Potassium iodate, which has been assigned to the perovskite structure, is highly birefringent and therefore not cubic. Several attempts were made to grow crystals of KIO_3 suitable for analysis but none were obtained which were useful, even with the microscope. The most striking point of Fig. 1 is the almost exact coincidence of the lines of CsI , KIO_3 and CsNO_3 , both in number and position, and to

³ Wyckoff, R. W. G., *Zeits. f. Krist.* **63**, 507 (1926).

⁴ A. N. Winchell, *Microscopic Characters of Artificial Minerals*, p. 208, John Wiley and Sons, New York, 1931.

⁵ Pauling and Sherman, *Zeits. f. Krist.* **84**, 213 (1933).

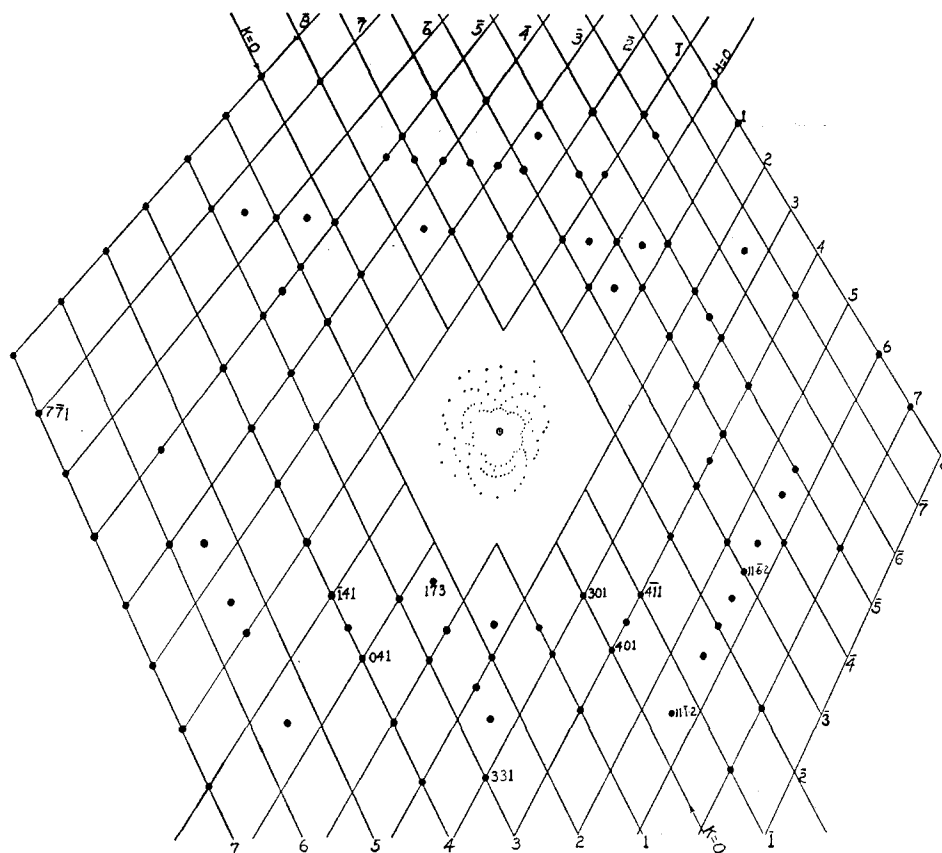


FIG. 2. Gnomonic projection of CsNO_3 . X-rays nearly parallel to c axis.

some extent in intensity. Very careful measurements showed a slight difference in position.

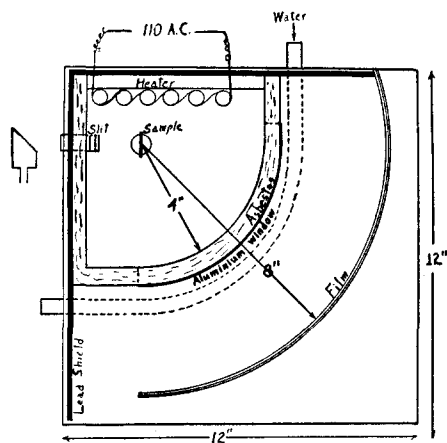


FIG. 3. Heated powder diffraction camera.

The authors therefore state that crystals giving an apparently cubic powder diffraction pattern are not necessarily cubic, as has been recognized for $\text{LiCl} \cdot \text{H}_2\text{O}$ ⁶ and that practical identity of spacings of lines on the pattern are not proof of identity unless the intensity is taken into account.

The "perovskite structure" can be applied only to perovskite which is most probably orthorhombic but has been used as a type of cubic symmetry. The use of the term in this manner has apparently been based only on similarity of powder patterns. Obviously the term should be discontinued or the term "perovskite pattern" applied to pseudo-cubic powder diffraction patterns.

⁶ S. B. Hendricks, *Zeits. f. Krist.* **66**, 131 (1927).