

Select contributions of H. D. Megaw: Structure – property relations in thermal expansion of crystals, and ferroelectrics

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What are structure-property relations all about?





Assistant Director of Research at the Cavendish Laboratory in Cambridge.

http://cwp.library.ucla.edu/Phase2/Megaw,_Helen@851234567.html

https://en.wikipedia.org/wiki/Helen_Megaw

Ferroelectricity in Crystals. Methuen, London 1957.

Crystal Structures: A Working Approach. W.B. Saunders Co., Philadelphia 1973.



"Appointed as the first lecturer in Structural Crystallography at Cambridge (1927) ... crystallographic techniques to organic molecules, starting with oestrin and sterol compounds including cholesterol in 1929, he analysed vitamin B1 (1933), pepsin (1934), vitamin D2 (1935), the sterols (1936), and the tobacco mosaic virus (1937), ... also worked on the structure of liquid water, showing the boomerang shape of its molecule (1933). With Dorothy Hodgkin in 1934, took the first X-ray photographs of hydrated protein. Max Perutz arrived as a student from Vienna in 1936 and started the work on haemoglobin."

Bernal and Megaw on hydrogen (and hydroxyl) bonding:

The Function of Hydrogen in Intermolecular Forces

Author(s): J. D. Bernal and H. D. Megaw

Reviewed work(s):

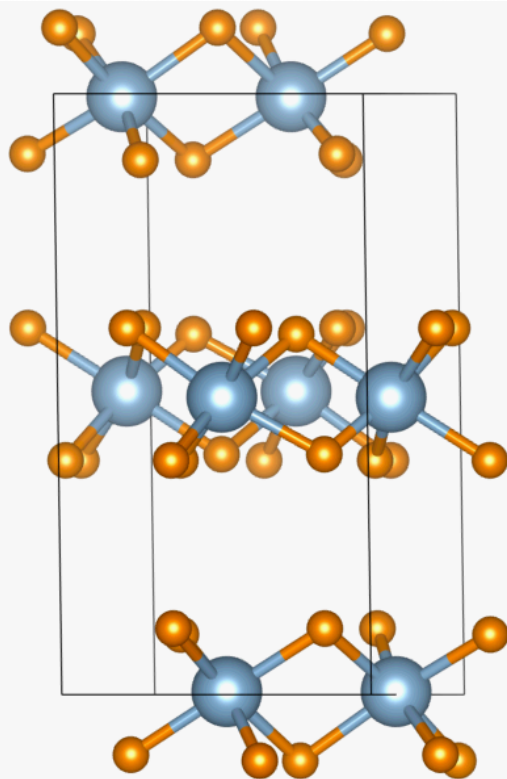
Source: *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, Vol. 151, No. 873 (Sep. 2, 1935), pp. 384-420

The Function of Hydrogen in Intermolecular Forces

By J. D. BERNAL and H. D. MEGAW

(Communicated by R. H. Fowler, F.R.S.—Received December 3, 1934—

Revised March 5, and July 9, 1935)



NATURE

DECEMBER 8, 1934

Cell Dimensions of Ordinary and 'Heavy' Ice

I HAVE recently made accurate determinations of the cell dimensions of crystals of ordinary and 'heavy' ice (D_2O). Single crystals were used. The apparatus consisted of a small Dewar flask mounted on the arcs of a Bernal photogoniometer, and filled with a mixture of acetone and solid carbon dioxide. A holder of copper wire attached to the bottom of the flask contained a capillary tube of Lindemann glass, into which a drop of water was sealed. The crystal was grown by inserting the glass tube into its holder in contact with the cooling mixture; its growth was observed with a polarising microscope, and it was thawed and grown again until a good single crystal was obtained. The direction of fastest growth was the normal to $(11\bar{2}0)$, so that this direction generally grew along the axis of the tube. There was a steep temperature gradient in the crystal; at the holder it was very nearly at $-78^\circ C.$, while its top, about 3.3 cm. above this, was at the melting point, and was in contact with a layer of liquid. The spacings could thus be determined at different temperatures.

Preliminary photographs showed that the structure of crystalline D_2O is the same as that of ordinary ice. The setting of the crystal was made by means of oscillation photographs. The exact spacings were determined from reflections at nearly 180° , recorded with a back-camera. For a , the plane $(50\bar{5}0)$ was used with copper $K\alpha$ radiation, for c , (0008) with cobalt $K\alpha$. The spacings were measured at $-66^\circ C.$ and at the melting-point. The results are given below, with an estimate of the probable limits of experimental error (values for D_2O at $0^\circ C.$ are calculated from those at $4^\circ C.$ by interpolation).

	Temp. $^\circ C.$	Ordinary ice (H_2O) (A.)	'Heavy' ice (D_2O) (A.)	Probable limits of error (A.)
Base of cell, a	-66	4.5085	4.5055	± 0.002
	0	4.5135	4.5185	± 0.0014
	4	—	4.5175	± 0.0014
Height of cell, c	-66	7.338	7.338	± 0.0035
	0	7.3521	7.3537	± 0.0012
	4	—	7.3552	± 0.0012

Gibbsite $Al(OH)_3$: Where are the hydrogen atoms?



The Thermal Expansions of Certain Crystals with Layer Lattices

Author(s): Helen D. Megaw

Reviewed work(s):

Source: *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, Vol. 142, No. 846 (Oct. 1, 1933), pp. 198-214

The Thermal Expansions of Certain Crystals with Layer Lattices.

By HELEN D. MEGAW, M.A., Yarrow Research Student of Girton College,
Cambridge.

(Communicated by A. Hutchinson, F.R.S.—Received May 5, 1933.)

[PLATE 2.]

The methods for the determination of linear expansion coefficients which are applicable to anisotropic substances fall into two main groups, the optical and the X-ray methods. Of these the former have hitherto been much more extensively used. They consist essentially in measuring the change in distance between two plane surfaces of the crystal. Thus, Fizeau* investigated a large number of crystals by an interferometer method, and much of the subsequent work on single crystals has been done by modifications of this method. An optical lever method was applied by Roberts† to the measurement of the expansion of single crystals of bismuth. The X-ray method determines directly the change in lattice spacing of the crystal.

Linear expansion coefficients can be measured with high accuracy, even when large crystals are not available.



Table II.—Expansion coefficients of calcite $\times 10^5$.

	Present experiment.	Fizeau.*	Benoit.†
Parallel to axis	2.53 ± 0.15	2.621	2.5135
Perpendicular to axis.....	-0.52 ± 0.07	-0.540	-0.5578

* 'C. R. Acad. Sci. Paris,' vol. 66, p. 1005 (1868).

† 'Trav. Mem. Bur. Int. Poids et Mes.,' vol. 6 (1888).

Measurements on calcite – already known from 1868 to show negative thermal expansion along one of the directions.

Table from the publication on previous page.

Table 2. Nb displacements and O–O edge lengths of octahedra in alkali niobates

Material	Phase and temperature	Relation of octahedron to symmetry of structures	Type of Nb displacement	Magnitude of Nb displacement (Å)	Relaxed edge lengths (Å)		Unrelaxed edge lengths (Å)		Difference e (Å)	Overall mean, l_m (Å)
NaNbO ₃	Phase <i>P</i> , orthorhombic, 20°C	Asymmetric	Two-corner approx. [100]	0.15	[001] 2.807 [001] 2.825 [100] 2.810 [100] 2.812 $s = -0.005$	2.816 2.811	2.756 2.799 2.770 2.817 2.786 2.831 2.798 2.825	2.796	0.018	2.802
NaNbO ₃	*Cubic, 640°C	Coincident	Central	0						2.787
Na _{0.975} K _{0.025} NbO ₃	Orthorhombic, 20°C (isostructural with phase <i>Q</i>)	Asymmetric	Two-corner approx. [100]	0.21 ± 0.07	(Mean of 4)	2.807 ± 0.010	(Mean of 8)	2.792 ± 0.005	0.015 ± 0.005	2.80
KNbO ₃	Orthorhombic, 20°C	One tetrad and two diads fixed	Two-corner [001]	0.20	[100] 2.802 [100] 2.894 [001] (2) $s = 0.012$	2.848 2.860	(4) 2.780 (4) 2.884			
KNbO ₃	*Tetragonal, 225°C	Three tetrads fixed	One-corner [001]	?	(8)	2.849	(4) 2.832	2.826	0.022	2.840
KNbO ₃	*Cubic, 425°C	Coincident	Central	0						2.841
LiNbO ₃	Rhombohedral 24°C	One triad and three diads fixed	Three-corner [0001]	0.26	Top (3) 2.879 Bottom (3) 2.719 Inclined (3) 2.801 Inclined (3) 2.840 $s = 0.021$	2.799 2.820 2.810		None	—	2.810

Bond lengths are accurate to about ± 1 in the last figure quoted, except where otherwise stated. Edge lengths for phases marked * have been calculated from the lattice parameters.

H. D. Megaw, The thermal expansion of interatomic bonds, illustrated by experimental evidence from certain niobates, *Acta Cryst.* A24 (1968) 589.

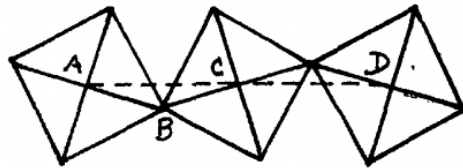


FIG. 1

Three hypothetical structures, illustrating different effects of expansion: (a) blocks having an expansion different from the matrix; (b) framework with tilted polyhedra; (c) blocks capable of tilting within a 'soft' matrix.

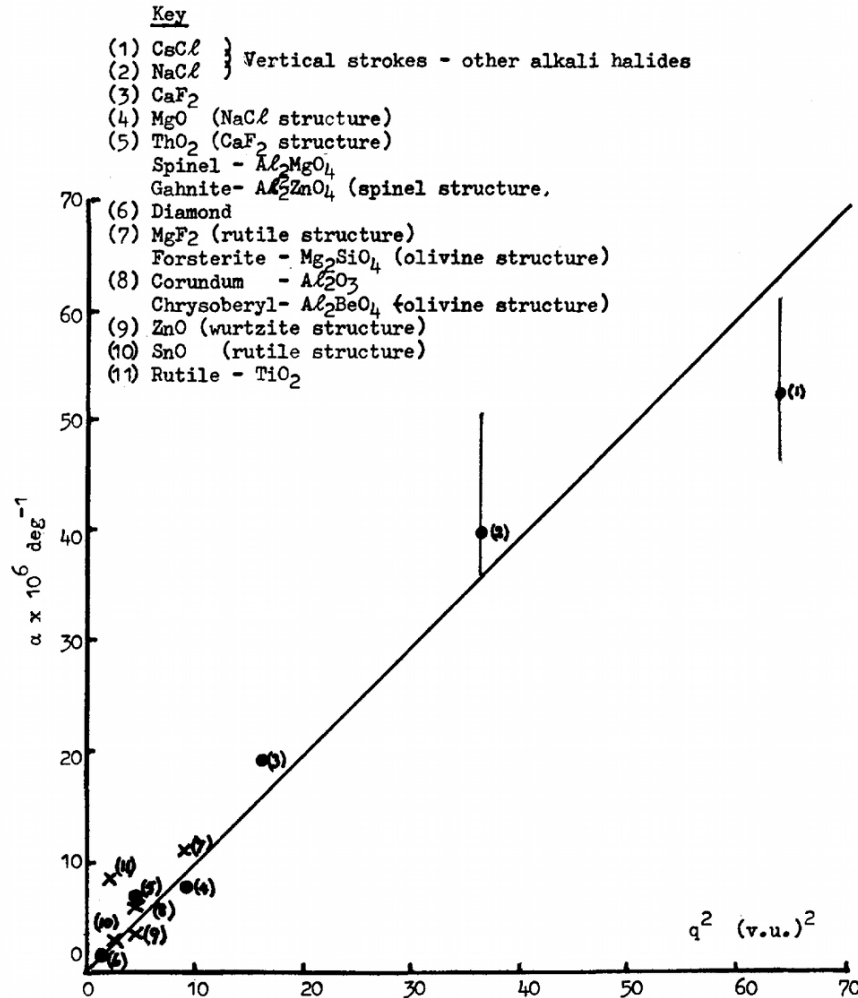
(ii) The structure shown in Fig. 1(b) consists of identical squares tilted with respect to one another by the angle $BAC = \phi$. If $AB = \ell$, $AD = a = 4\ell \cos \phi$. Now suppose each square expands homogeneously, and also, independently, the tilt angle changes with temperature: the overall linear expansion coefficient along AD is

$$\frac{1}{\ell} \frac{d\ell}{dt} - \sin \phi \frac{d\phi}{dt} \quad (2)$$

The first term is the expansion coefficient of the square itself, the second a consequence of the crumpling of the framework.

H. D. Megaw, Crystal structures and thermal expansion, Mat. Res. Bull. 6 (1971) 1007-1018.

Megaw on thermal expansion: Relations to bond strength



$q = \text{CN}/\text{charge}$, referred to by Megaw as Pauling valence

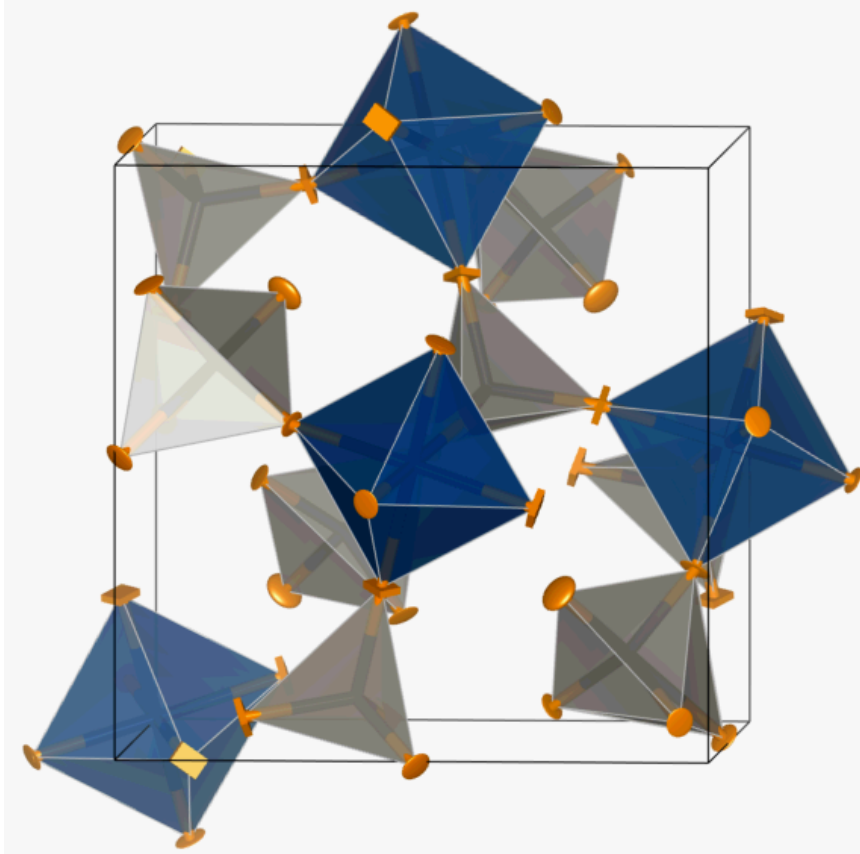
$q = 8$ for CsCl

$q = 6$ for NaCl

$q = 4$ for CaF₂

These are all examples of linear expansions only, with no angular changes.

H. D. Megaw, Crystal structures and thermal expansion, Mat. Res. Bull. 6 (1971) 1007-1018.



Zr in octahedra and W in tetrahedra. 50% thermal ellipsoids displayed.

J. D. Jorgensen, Z. Hu, S. Teslic, D. N. Argyriou, S. Short, J. S. O. Evans, and A. W. Sleight, Negative thermal expansion from 0.3 to 1050 Kelvin in ZrW_2O_8 , *Phy. Rev. B* 59 (1999) 2155-225.

Crystal Structure of Barium Titanate

It is well known that barium titanate belongs to the group of compounds having structures of the perovskite type¹. The ideal perovskite structure (*G5* in the "Strukturbericht") has a simple cubic lattice, with one formula-weight per cell, the atomic parameters being as follows: 2-valent cation, (0,0,0); 4-valent cation, ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$); oxygens, ($0, \frac{1}{2}, \frac{1}{2}$), ($\frac{1}{2}, 0, \frac{1}{2}$), ($\frac{1}{2}, \frac{1}{2}, 0$). It was early recognized² that for many of these compounds, including perovskite (CaTiO₃) itself as well as barium titanate, the structure was not truly cubic, but was actually a slightly deformed modification of it. Perovskite itself is generally believed monoclinic; the structure has recently been determined in detail by Naray-Szabo³, who finds a monoclinic unit cell with all its edges doubled relative to the unit cell of the ideal structure. No detailed work on barium titanate has hitherto been published, and it was thought of interest to investigate it. Powder photographs of the synthetic material taken in a 19 cm.-diameter camera with copper *K* α radiation provided the data for determining the structure.

The structure is tetragonal, the dimensions of the unit cell at 20° C., for a typical sample of material,

being as follows: $a = 3.9860 \pm 0.0005$ kX., $c = 4.0263 \pm 0.0005$ kX., $c/a = 1.0101 \pm 0.0002$. This cell contains one formula-weight, BaTiO₃. The atomic parameters are the same as in the ideal cubic structure. The relationship between the tetragonal and cubic structure is close; the tetragonal unit cell may be simply derived from the cubic by stretching it homogeneously by about 1 per cent along one tetrad axis, which becomes the *c* axis.

This close relationship suggests that a transition to the cubic structure may occur at higher temperatures. This was verified from photographs taken with a high-temperature camera. At 200° C., barium titanate has the ideal cubic structure, with $a_0 = 4.0040 \pm 0.0005$ kX.

Further work is in progress.

I wish to express my gratitude to Sir Lawrence Bragg for allowing me the use of the high-temperature camera in his laboratory. I wish also to thank Mr. J. A. M. van Moll (head of the Material Research Laboratory) and the directors of Philips Lamps, Ltd., for permission to publish this work.

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Feb. 24.

¹ Goldschmidt, V. M., "Geochem. Verteilungsgesetze d. Elem.," 8, 153 (1927).

² *ibid.*, and also 7, 37 (1926).

³ Naray-Szabo, I., *Naturwiss.*, 31, 202 (1943).



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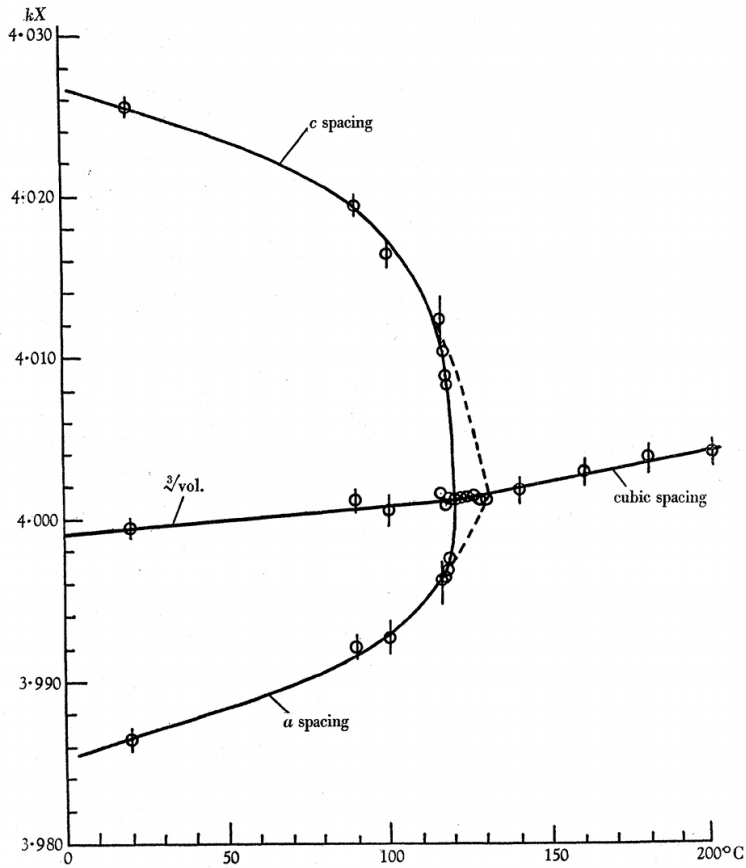
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³ Naray-Szabo, I., *Naturwiss.*, 31, 202 (1943).





Cell parameters and thermal expansion coefficients.

H.D. Megaw, Temperature changes in the crystal structure of barium titanium oxide, Proc. R. Soc. Lond. A 189 (1947) 261-283.

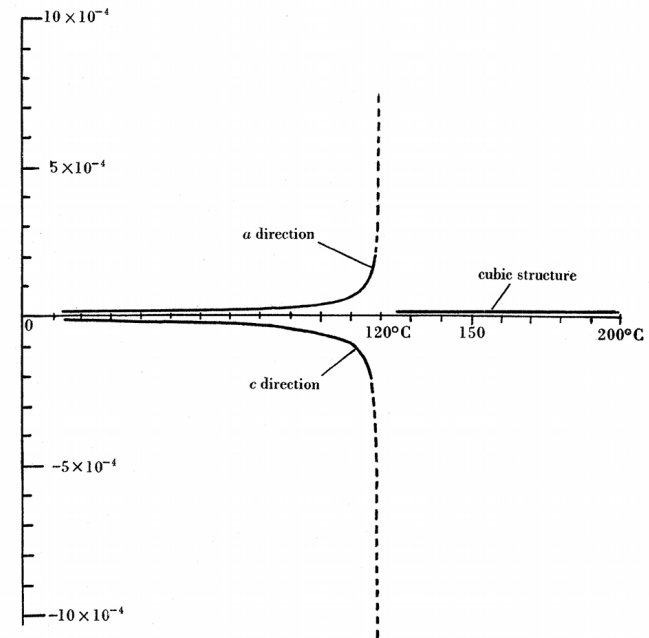


FIGURE 4. Linear expansion coefficients of BaTiO₃.

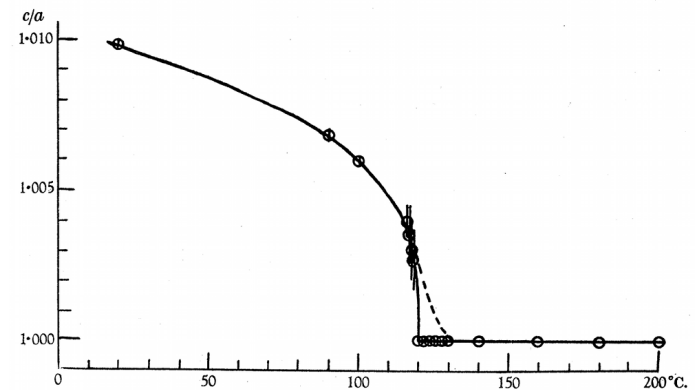


Table 2. Modifications of perovskite-type structures, and their transition temperatures

	CaTiO ₃	SrTiO ₃	BaTiO ₃	NaNbO ₃ *	KNbO ₃	NaTaO ₃	KTaO ₃	RbTaO ₃
High temperatures			Cubic, single	Cubic	Cubic, single			Cubic
				640° C.				
				480° C.				
				Tetragonal, multiple	Tetragonal, single			
			120° C.	370° C.	225° C.	475° C.		245° C.
Room temperature	Orthorhombic, multiple	Cubic, single	Tetragonal, single	Orthorhombic, multiple	Orthorhombic, single	Orthorhombic, multiple?	Cubic	Tetragonal, single?
Low temperatures		No transition to 1.3° K.	0° C.	No transition to 100° K.	No transition to 223° K.			
			Orthorhombic, single					
			183° K.					
			Rhombohedral, single					
							About 13° K.	
							?	

* Different values are given for the transition temperatures (Wood, 1951; Matthias & Remeika, 1951; Vousden 1951a).

H. D. Megaw, Origin of ferroelectricity in barium titanate and other perovskite-type crystals, Acta Cryst. 5 (1952) 739.

"The origin of ferroelectricity is attributed to a small change of bond character occurring in a structure whose geometry is compatible with either ionic or homopolar binding."



The BaTiO₃ structures

