Helen D. Megaw (1907–2002) and Her Contributions to Ferroelectrics

HELEN D. MEGAW was a pioneer in crystallography where her work on perovskites had a great impact on the research on ferroelectrics and beyond. In addition to her scientific discoveries, she was also a mentor and role model to many people in the field. This article celebrates her life and the numerous scientific contributions to the structures of ferroelectric materials.

Helen Dick Megaw was born on June 1, 1907, into a most distinguished and influential Northern Irish family. Her father, Robert Dick Megaw, was a famous Chancery Judge in the High Court of Justice of Northern Ireland and an Ulster politician. Also, her uncle, Major-General Sir John Wallace Dick Megaw, was a director of the Indian Medical Service, while one brother built the Mersey tunnel (in Liverpool, U.K.), the Dartford tunnel (London), the Victoria underground line (London), and Battersea (London) power station. Another brother, Sir John Megaw, was a Lord Justice in the Court of Appeal, and one of her sisters researched diet and health in the 1930s and marriage laws in Uganda in the 1950s. A most extraordinary family background.

Helen was born in Dublin, Ireland, where she attended the Alexandra School from 1916 until her family moved to Belfast in 1921 just before the partition of Ireland. After a brief period at the Methodist College, Belfast, she went to Roedean School, Brighton, England, between 1922 and 1925. One of her aunts was secretary to the Mistress of Girton College, Cambridge (one of the only two Cambridge Colleges at the time exclusively set up for women: the College like all others in Cambridge now accepts both men and women) and Helen's ambition was to study there. She won an exhibition[1] to the College in 1925 but for financial reasons decided to go to Queen's University, Belfast. The next year, she won a scholarship, and this time, it proved possible for her to take up a place at Girton. Initially, she had intended to read Mathematics, but she had enjoyed Chemistry at school, and on her teacher's advice, she opted for Natural Sciences so that she could study both science and mathematics. She thought that the regulations required her to study three subjects, and she planned to study chemistry, physics, and mathematics. However, her Director of Studies, Miss M. B. Thomas, explained that she was required to study three *experimental* subjects (mathematics being an optional extra), and she advised Megaw to choose mineralogy as her third experimental subject. Had Helen known that she could have selected geology instead of mineralogy, she would have opted for geology, and, in all probability, she would not have become a crystallographer! Having achieved a Class I in Part I of the Natural Sciences Tripos[2] in 1928, she then specialized in physics, obtaining a Class II in Part II in 1930. When Ernest Rutherford at the Cavendish Laboratory told her that there was no opportunity for her to do post-graduate work in the Physics department, Miss Thomas suggested that she approach Prof. Arthur Hutchinson, whose Department of Mineralogy had a strong crystallographic tradition. So, it was that she became a research student under the renowned, and some would say infamous, John Desmond Bernal, investigating the thermal expansion of crystals, and the atomic structure of ice and the mineral hydrargillite (a hydroxide of aluminum). One of Bernal's students at the same time was the young Dorothy Crowfoot, later to become famous as the Nobel Prize winner Dorothy Hodgkin, and Helen and Dorothy became firm friends.

Fig. 1. Helen D. Megaw with her oscillation camera.

Bernal was a stimulating influence on Helen and happily confirmed her interest in crystals. Her choice of crystallography was a wise one, because it was the one scientific discipline then, thanks principally to W. H. and W. L. Bragg, which had already established itself as a place in which both men and women could engage on an equal basis, and she never, or rarely, was aware of any form of discrimination. She started work on the structure of the mineral hydrargillite, a form of $Al(OH)_3$. Fig. 2 shows a photograph of a model of its crystal structure. Although rather rough, having seen better times, this model was her first crystal model constructed with help from Dorothy Hodgkin in 1934. Megaw's main Ph.D. work with Bernal was a study of the crystal structures of ice. Helen's accurate and demanding investigation of ice and

Digital Object Identifier 10.1109/TUFFC.2020.3035268

[1]This is something peculiar to Oxford and Cambridge colleges. Particularly good students can be awarded an exhibition which usually gives them extra privileges in the College; see https://en.wikipedia.org/wiki/Exhibition_(scholarship).

[2]See https://en.wikipedia.org/wiki/Tripos for an explanation of Tripos.

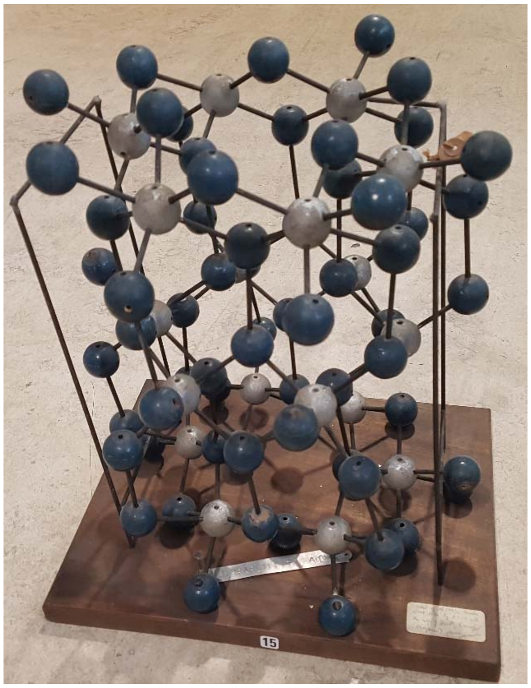

Fig. 2. Ball and spoke model of the crystal structure of hydrargillite 1934.

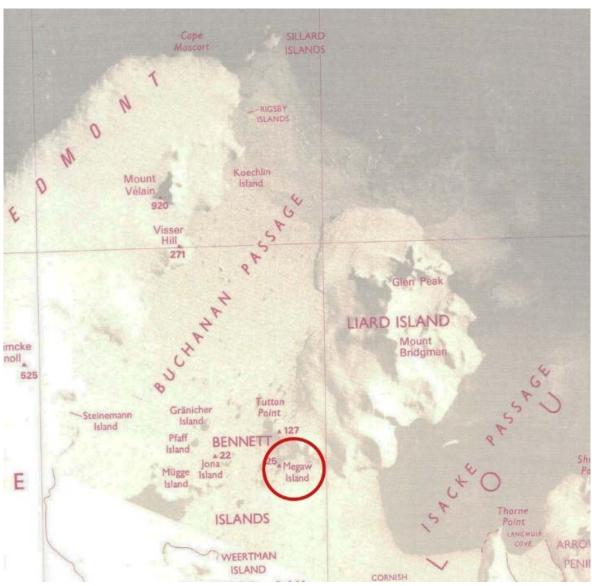

Fig. 3. Location of Megaw Island in Antarctica.

heavy ice showed that the hydrogen atoms were involved in bonding between two oxygens. She and Bernal surveyed the known structures of hydroxides and of water and concluded that there were two types of hydrogen bonds. In one kind, found in ice, the hydrogen oscillates between two positions, each being closer to one of the oxygen atoms than the other. In the other type, the hydrogen is bonded more strongly to one of the two oxygen atoms. In honor of her discoveries of the nature of ice, an island in Antarctica was named Megaw Island in 1962 (Fig. 3).

It is often said that it was Bernal who first suggested that X-ray photographs of biological crystals could be taken

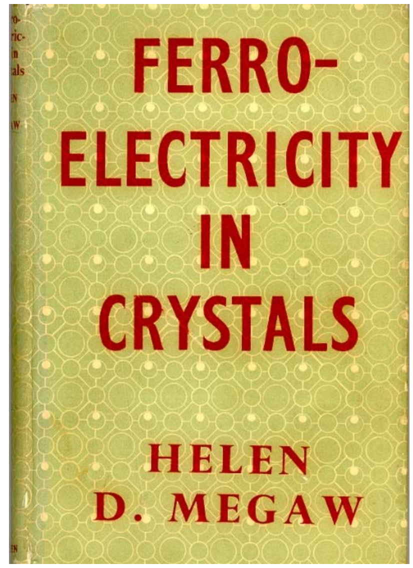

Fig. 4. Helen D. Megaw's classic book on ferroelectricity.

by encapsulating them in a mother-liquor in a glass tube, the technique that is often used to the present day. However, Helen once told the author that she had given the idea to Bernal first, as this was the technique that she had already mastered for her work on ice.

In 1934, Helen spent a year with Prof. Hermann Mark in Vienna and then moved to work briefly under Prof. Francis Simon at the Clarendon Laboratory, Oxford. This was followed by two years of school teaching before taking up a position at Philips Lamps Ltd. in Mitcham in 1943. It was here that she worked out the crystal structure of a significant industrial material, barium titanate, which is used in capacitors, pressure-sensitive devices, and in a variety of other electrical and optical applications. This material, which crystallizes in the so-called perovskite structure, belongs to the class of materials known as ferroelectrics, discovered initially around 1935. Because of its strategic military importance, much of the work was secret, and Helen was only allowed to publish her work on the structure provided that she did not mention its useful properties! This structure is so famous and important that Helen's name is permanently associated with it and with perovskite structures in general. In the ferroelectrics community, Helen's contributions are notably recognized, and her book *Ferroelectricity in Crystals* published in 1957 was the first of its kind and soon became a classic text (Fig. 4).

In 1945, she moved to Birkbeck College London, once again to work with Bernal, and in the following year, she was appointed to a post in the Cavendish Laboratory, Cambridge, where she remained for the rest of her scientific life. A second book followed years later titled *Crystal Structures: A Working Approach*, an excellent text that illustrates well her unique approach to describing the architecture of crystals. Her later detailed studies of the structures and phase transitions in $KNbO_3$, $NaNbO_3$, $LiNbO_3$, and Ca_2NbO_7, including the change in atomic vibrations near a transition temperature,

Fig. 5. Outside the Cavendish Laboratory, Cambridge. Front left to right: Unknown, A. D. Yoffe, Helen D. Megaw, W. H. Taylor, Sir Neville Mott, P. J. Brown, L. M. Brown. Back left to right: T. R. Thornley, unknown, C. N. W. Darlington.

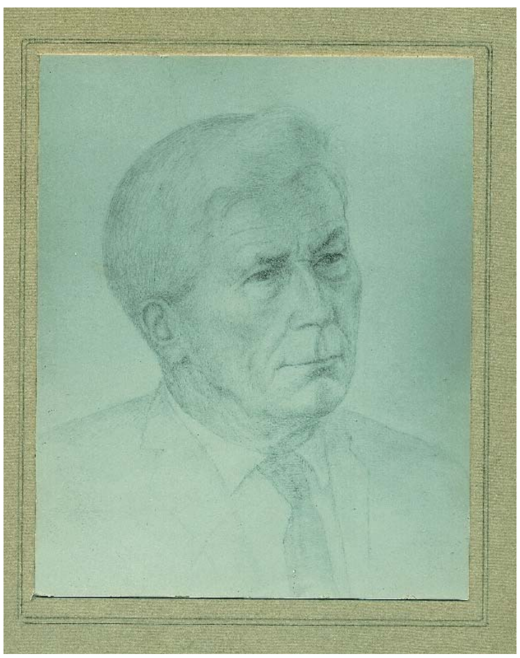

Fig. 6. WHT.

have contributed much to the understanding of the structural basis of ferroelectricity.

The Cavendish Laboratory was then under the leadership of the Nobel Laureate Sir William Lawrence Bragg, and as a result, Helen found herself at a place where many important and well-known crystallographers would pass through. She was there during the exciting double-helix days of Crick and Watson and the research by Perutz and Kendrew on hemoglobin and myoglobin. However, she remained loyal to her chosen field of mineralogy and inorganic crystals. Fig. 5 shows Helen with some members of staff and students at the Cavendish around 1968.

In addition to her interest in the structures of ferroelectrics, by a suggestion of William Hodge Taylor (often known simply as WHT), her immediate supervisor at the Cavendish Laboratory (Fig. 6), she took up an interest in the crystal structures of feldspars. These complicated materials make up most of the earth's and moon's surface and are therefore of considerable significance in the field of earth sciences. The first structure determination had been carried out by WHT before World War II, but such is the complexity of this class of materials, there remained a great deal of unknown science to discover. Feldspars are aluminosilicates with the general formula AT_4O_8 where A is most commonly calcium, sodium, or potassium and T represents aluminum and silicon present in the correct proportions to balance the charges on the A ions and the oxygens. Thus, albite has the formula $Na(Si_3Al)O_8$, anorthite $Ca(Si_2Al_2)O_8$, and orthoclase, $K(Si_3Al)O_8$. The plagioclase feldspars form a chemical series whose formulae may be written $Na_{1+y}Ca_y(Si_{3-y}Al_{1+y})O_8$ or more simply An_yAb_{1-y}, where Ab is albite and An anorthite. Plagioclase compositions appear homogeneous when examined using an optical microscope; there is no evidence of separation into domains of albite and orthoclase. However, X-ray diffraction patterns in the composition range $An_{30}Ab_{70}$ to $An_{70}Ab_{30}$ show diffracted beams, called "non-Bragg" reflections, which cannot occur in perfectly ordered crystals. Megaw, in three papers published in the *Proceedings of the Royal Society* in 1960, showed that the arrangement of "building blocks" in these crystals was disordered. She used diffraction theory to relate the positions and intensities of the non-Bragg reflections to the probability of the occurrence of fault planes in the structure and to the orientation of these planes within the structure. Knowledge of the detailed structural state of a plagioclase specimen is important because it allows the temperature of crystallization and the subsequent thermal history of the rock in which it occurs to be deduced. One of her discoveries in connection with feldspars illustrates a special and unique ability. Helen could visualize crystal structures entirely in her head. She never used computers but instead was able to see the atomic arrangements. For instance, if one asked her what a particular structure looked like down a specific direction she would think for a few moments and then draw it! Thus, she identified a special structural feature in feldspars involving rigid tilted tetrahedra which she likened to a "crankshaft." By cooperative tilting, this crankshaft can be closed up or extended relatively easily. As a consequence, the distribution of Al and Si in the tetrahedral sites has only a small effect on the bulk elastic moduli of plagioclase feldspars.

In the years after the war, the economic situation in Britain was dire, and recovery was slow. This was a time of much gloom and depression. The government decided that the nation's spirits would be lifted by holding a special festival in 1951, the so-called Festival of Britain. The idea was to create a series of country-wide events pointing to the future, with a large exhibition on the South Bank of the Thames in London. (The only remaining building from that exhibition today is the Festival Hall.) Helen had the brainwave to suggest that designs based on Crystallography could be used as decorations throughout the Festival site. She got several crystallographers, including Lawrence Bragg, Kathleen Lonsdale, and Dorothy Hodgkin to join in with creating the designs, which were then submitted to the Council of Industrial Design. These were then used in the textiles and other materials used at the Festival, including in the foyer of the Regatta Restaurant. The

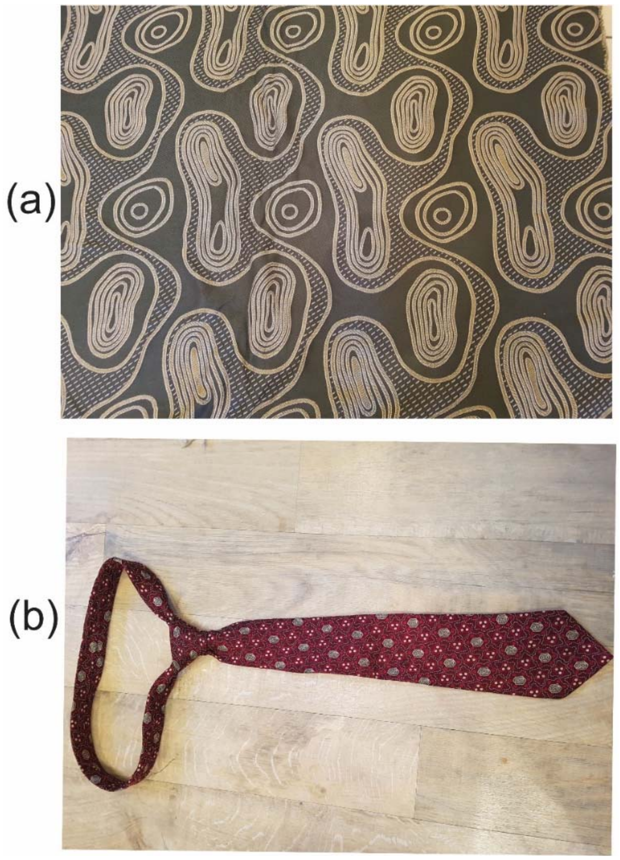

Fig. 7. Two examples of textile designs based on crystallographic structures by Helen D. Megaw.

carpets, curtains and table cloths, the knives and forks, glasses, and so on—all were decorated with features based on crystal structures.

Fig. 7 shows one of the popular textiles produced based on Helen's structure of afwillite and a tie with Dorothy Hodgkin's insulin structure. Today, many of these objects are kept at the Victoria and Albert Museum in London; more information can be found in the Art and Design archives at http://www.vam.ac.uk/__data/assets/pdf_file/0015/250125/megaw_aad_1977_03_20141020.pdf.[3]

In 1958, Helen was invited to Penn State by Ray Pepinsky, and she took the opportunity to attend the American Crystallographic Association meeting in Ann Arbor to present a paper on KH_2PO_4. She reported later

> *After it, Pepinsky, in the discussion, made a criticism so fierce that the chairman said he thought I should have the right to reply at the end of the session. Though very grateful to the chairman, I was not seriously worried. I was confident that my own ideas were right, and thought Pepinsky was quite wrong. But I remember that later someone in the audience said to me, "Are you still going to State College?" Well, I went to State College and spent a very enjoyable summer. It was worth the opportunities it gave me to travel, see something of America, meet people and see other labs, rather than for any work I actually did there!*

[3]There is a beautiful book *From Atoms to Patterns* by Lesley Jackson, where the whole story has been recounted with many excellent photographs of the crystallographic designs.

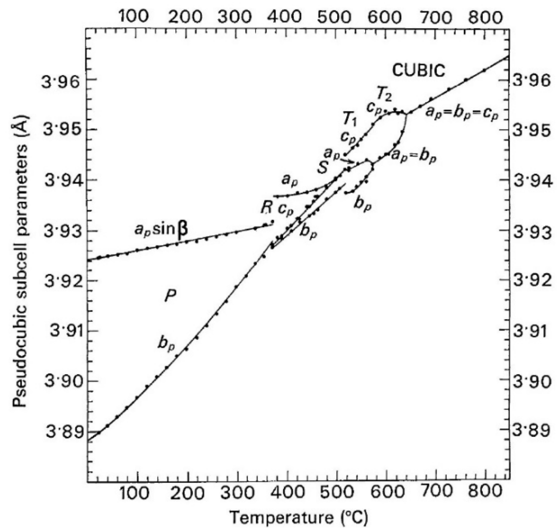

Fig. 8. Lattice parameters as a function of temperature for a crystal of $NaNbO_3$ showing a complex series of phase transitions.

Fig. 9. Helen D. Megaw in her garden in Ballycastle, Northern Ireland together with one of her ex-student, Christine McKie (formerly Kelsey).

In her last few years at the Cavendish, starting in 1969, she and the author worked together, initially on the study of phase transitions in the perovskite $NaNbO_3$. This had a sequence of at least seven different phases, depending on temperature. She had already produced a graph of the lattice parameters as a function of temperature based on earlier work, and much of it was guesswork. The author's job was to build an X-ray camera with a reliable high-temperature system. With this, it was possible to derive a quite accurate sequence of the phase transitions (Fig. 8), which in the event was very close to Helen's original "guesswork."

In 1972, Helen retired to her home in Ballycastle, County Antrim, Northern Ireland (Fig. 9), to pursue her other interest, gardening, although she maintained her interest in ferroelectrics and continued to act as a journal referee.

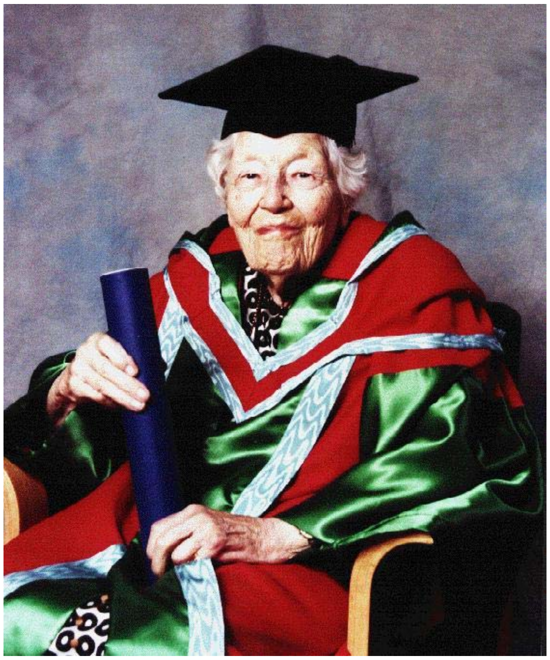

Fig. 10. Helen D. Megaw in 2000 with honorary degree at Queen's University, Belfast.

In 1989, Helen became the first woman to be awarded the prestigious Roebling Medal of the Mineralogical Society of America. Bob Newnham (Penn State) wrote at the time:

> *A number of American crystallographer-mineralogists were trained at Cambridge, and all of us remember her meticulous style of teaching symmetry and crystal chemistry. Crystal Structures–A Working Approach, her last book, published in 1973, contains many of the concepts and interesting home problems presented in her classes. She had a kind heart and a patient way with students that cause many of us to look back with great fondness on our days at the Cavendish. Along with Kathleen Lonsdale and Dorothy Hodgkin, Helen Megaw is one of the grand old British school of women crystallographers who serve as role models for many of us—men and women alike. I am proud to have been one of her students.*

In 2000, at the age of 93, she was awarded an honorary degree at Queen's University, Belfast (Fig. 10).

In a citation for the honorary degree in 2000, Prof. Ruth Lynden-Bell recalled those early days of crystallography research:

> *It is difficult for us to imagine the scientific environment in the nineteen thirties. It was a time of depression with little money and few jobs. Science departments were much smaller and more intimate. X-ray crystallography was a new science which attracted a number of young women such as Dr. Megaw who became distinguished scientists. In those pioneering days preparation of crystals and collection of data was more difficult and more skilled than it is today. Another big difference, which today's graduates may find hard to imagine, was that there were no computers and the tedious and detailed calculations which lead from the brightness of spots on a photographic plate to a three-dimensional crystal structure were all done by hand. Dr. Megaw was one of the pioneers in this field.*

Helen died in Ballycastle on February 26, 2002, at the grand age of 94.

I. Some Important Publications

H. D. Megaw, "Cell dimensions of ordinary and 'heavy' ice," *Nature*, vol. 134, no. 3397, pp. 900–901, 1934.

J. D. Bernal and H. D. Megaw, "The function of hydrogen in intermolecular forces," *Proc. Roy. Soc. London. Ser. A, Math. Phys. Sci.*, vol. 151, no. 873, pp. 384–420, 1935.

H. D. Megaw, "Crystal structure of barium titanate," *Nature*, vol. 155, no. 3938, pp. 484–485, 1945.

H. D. Megaw, "Origin of ferroelectricity in barium titanate and other perovskite-type crystals," *Acta Crystallographica*, vol. 5, no. 6, pp. 739–749, 1952.

H. D. Megaw, "Order and disorder. I. Theory of stacking faults and diffraction maxima," *Proc. Roy. Soc. London. Ser. A, Math. Phys. Sci.*, vol. 259, no. 1296, pp. 59–78, 1960.

H. D. Megaw, "Order and disorder. II. Theory of diffraction effects in the intermediate feldspars," *Proc. Roy. Soc. London. Ser. A, Math. Phys. Sci.*, vol. 259, no. 1297, pp. 159–183, 1960.

H. D. Megaw, "Order and disorder. III. The structure of the intermediate plagioclase feldspars," *Proc. Roy. Soc. London. Ser. A, Math. Phys. Sci.*, vol. 259, no. 1297, pp. 184–202, 1960.

A. M. Glazer and H. D. Megaw, "Studies of the lattice parameters and domains in the phase transitions of $NaNbO_3$," *Acta Crystallographica*, vol. 29, no. 5, pp. 489–495, 1973.

II. Books

Ferroelectricity Crystals. Methuen, London, U.K., 1957.

N. V. O. Uitgevers-Maatschappij, *Crystallographic Book List*. Domstraat, The Netherlands: International Union of Crystallography Commission, 1972.

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

Acknowledgment

This article was originally published on the American Crystallographic Association website at https://history.amercrystalassn.org/biography—megaw, but the author maintained ownership of the content to allow publication in this Special Issue.

Mike Glazer
Physics Department
University of Oxford
Oxford OX1 3PU, U.K.