Ferroelectrics
1975, Vol. 9, pp. 151-153

REMINISCENCES OF W. G. CADY AND THE EARLY HISTORY OF FERROELECTRICITY

HANS JAFFE

3590 Woodridge Road, Cleveland, Ohio 44121, U.S.A.

(Received February 3, 1975)

Prof. Walter G. Cady (1874-1974). Photograph, courtesy of Prof. R. Bruce Lindsay.

On 9 December, 1974, Professor Walter Guyton Cady, the inventor of Frequency Control by quartz crystals, died one day short of his 100th birthday. Twelve years before he had returned to live in the fine old home of his birth on Brown University Hill in Providence, Rhode Island, U.S.A.

Early in November 1935 the writer, just arrived from threatened Europe, was met by Professor Cady at the Meriden Railroad Station to interview for a research assistantship in Physics at Wesleyan University. I had heard of Cady as a key name in piezoelectricity, but as a Goettingen Ph.D. of 1934 I had background neither in the practice of radio communications and electroacoustics nor in the underlying theory of elasticity. In Professor Cady I found an inspiring and patient teacher. My principal task turned out to be the collection and organization of material for the treatise Piezoelectricity,[1] and especially on Rochelle Salt which was as yet the only known ferroelectric (or rather seignette-electric in those days).

This subject was not entirely new to me. At Berlin in 1929 I had heard a talk by A. Joffé on the studies of Rochelle Salt in his Leningrad Institute by I. V. Kurtchatov and coworkers. Prof. Joffé described the phenomenon of spontaneous dielectric polarization in Rochelle Salt and suggested that the mysterious exchange forces just discovered by Heisenberg might be manifested by ferromagnetism in paramagnetic materials, by spontaneous dielectric polarization in materials containing electric dipoles, and perhaps by yet other phenomena of internal ordering. After the lecture, F. London informed the distinguished guest that exchange forces acted *only* between magnetic spins. Indeed, it was soon recalled that the typical magnitude of electric dipoles is ample to cause self-polarization in polar solids and liquids—the $4\pi/3$ catastrophe of early solid state physics. The quandary was the apparent non-existence of ferroelectricity (as of 1910), not its discovery in 1920.

In 1932 A. von Hippel gave a colloquium on Rochelle Salt at Goettingen. He showed a 2 kg single crystal donated by the Brush Company of Cleveland and shocked the Professor of Crystallography, V. M. Goldschmidt, by proposing to sacrifice this beautiful creation to experiments. Von Hippel started a program more concerned with dielectric relaxation than with ferroelectricity. The Russian workers likewise were convinced of cooperative spontaneous polarization in Rochelle Salt only after experimental proof that the dielectric hysteresis and high dielectric constant were not due to space charges and blocking layers. Such caution is advised even today for alleged ferroelectricity in the presence of inhomogeneous electric conductivity, especially in polycrystalline bodies!

My work at Wesleyan began with a study of the classical work of F. Pockels[2] on electrooptic properties of piezoelectric crystals. Pockels discovered a substantial Kerr (quadratic) electrooptic effect for field in the a-direction of Rochelle Salt, and very large but variable and time-dependent linear electrooptic and piezoelectric effects. He might well have discovered ferroelectricity had he not been misled by an erroneous low dielectric constant in the literature. No work on the electric properties of Rochelle Salt was reported in the next 20 years.

A new era was initiated by a meeting in June 1917 between a European antisubmarine task group led by Ernest Rutherford and American scientists. Cady was invited in view of his practical experience in magnetism, but on hearing of P. Langevin's work with piezoelectric quartz ultrasonic transducers he saw at once that here was the future of underwater signalling and detection.[3] His whole life's work acquired its direction from this encounter. While the European teams stuck to quartz, several Americans, including Cady, turned to the much more sensitive Rochelle Salt. Cady in particular was successful in developing a Rochelle Salt microphone capable of detecting underwater sound signals from as far as 3 miles away. In a report of May 1918 Cady described non-linear piezoelectric response of Rochelle Salt: quadratic at low stress and then approaching saturation. J. A. Anderson, also involved in the submarine effort, described similar response to applied electric field.

These reports were "secret" and could not be retrieved by Prof. Cady when he worked on his book in the 1930's! Fortunately, however, they were seen by some physicists, including W. F. G. Swann and Joseph Valasek. The latter, in his first paper,[4] summarizes the observations of Cady and Anderson, and writes: "It appears, however, that these results can be accounted for by a hysteresis in the crystal similar to ferromagnetic hysteresis, in a manner suggested by Prof. W. F. G. Swann, as follows. . . .". Valasek's second paper[5] starts with the sentence: "Recently the writer described some experiments on the dielectric and piezoelectric properties of Rochelle Salt, which were made for the purpose of correlating and explaining the effects observed by Cady and Anderson." Valasek's own contributions in these two papers were well-defined hysteresis loops, measurement of dielectric constants in the order of 1000, and the discovery that the anomalously high dielectric and piezoelectric effects occurred only between about −20 and +20°C, which he termed Curie points. Valasek is thus justly regarded as the discoverer of ferroelectricity, but there is clear lineage from Cady and Anderson to Valasek and all who followed him.

In the 1920's Prof. Cady concentrated on the study of quartz resonators and their application to frequency control. The only significant further U.S. contribution to Rochelle Salt in this decade was the industrial development of crystal growth and crystal element fabrication by C. B. Sawyer and associates in the Brush Laboratories who also pioneered in the application of CR tubes to hysteresis loop study[6]. They laid the foundation for a unique industry which flourished for some 25 years. By 1940 more than 90% of the world's phonographs contained Brush "Bimorph" Rochelle crystal elements.

Scientific interest in Rochelle Salt spread from 1930 on. Hans Mueller, a student of P. Scherrer at Zurich, came to M.I.T. about 1932 and quickly became the leader by exhaustive dielectric and optic measurements over wide ranges of temperature and field strength. He developed a phenomenological theory which demonstrated that slow variation of just the linear term of molecular polarizibility with temperature could account for the existence of Curie points and the pronounced nonlinearities observed near them.[7] Much of my early effort at Wesleyan was the digestion of Mueller's extremely condensed presentation. A minor task left to us was the elucidation of symmetry and phase relations.[8] Physicists in those days accepted crystallographic classification as a fiat. Rochelle Salt *was* orthorhombic, class V^d, and the observed pyroelectric effect "forbidden". Experimental work on Rochelle Salt at Wesleyan was concerned primarily with elastic and piezoelectric measurements relevant to transducers applications. It was, however, the work of W. P. Mason at Bell Laboratories[9] which solidly established the interrelation of dielectric, piezoelectric, and elastic constants in Rochelle Salt and materials of high piezoelectric coupling in general.

I left Wesleyan in 1939 and joined the Brush Development Co. in 1940, a natural move for Cady's research assistant. My assignment was succinct: To find a crystal as stable and rugged as quartz, and as strongly piezoelectric as Rochelle Salt. Our first answer was the ADP crystal, ammonium dihydrogen phosphate. It was, of course, the work of Busch and others at Zurich which guided us to the dihydrogen phosphates, but to our surprise we found ADP, which becomes antiferroelectric, to have a higher piezoelectric effect than KDP which is ferroelectric at low temperature.

ADP fell far short of my assignment; it rather was the geometric mean between the two "old" crystals in respect to ruggedness on the one hand and piezoelectric coupling on the other. It was found quite satisfactory for underwater acoustics, but inadequate in piezoelectric coupling and dielectric constant for air-acoustic applications. Professors Cady and Karl van Dyke at Wesleyan were deeply committed to the underwater war effort and gave much encouragement to our endeavor.

The War delayed publication of Cady's "Piezoelectricity" until 1946. It was completed a little too early to mention barium titanate, but a chapter on new developments was included in a revised paperback edition in 1964.[1a] The discovery that polycrystalline ferroelectrics of cubic reference structure could be rendered remanently polar and piezoelectric did not come from Prof. Cady's school. Involvement with Rochelle Salt was actually an obstacle to this discovery since its domains cannot be permanently reoriented due to their spontaneous shear strain.[10] The useful piezoelectric effect of Rochelle Salt is that present in the non-polar reference structure, albeit enhanced by the vicinity of the Curie point.

After retiring from Wesleyan in 1950 Cady spent 12 years in Pasadena where he experimented on ultrahigh frequency sound waves in the basement of the Cal.Tech. Physics Department. After his return to Providence he continued to work and publish on piezoelectric design problems. He developed a piezoelectric ceramic accelerometer when past 90 and obtained a patent on it in 1973. After his death, his daughter-in-law, Mrs. Helen Cady, wrote: "It was sad that he did not live to receive the honors that were coming to him on (his 100th birthday), but I have the feeling that he no longer wanted to go on living. The only thing I ever heard him complain of was that he could no longer concentrate enough to work on his beloved physics."

Professor Cady built his own monument with his "Piezoelectricity". It combines the wealth of practical information worthy of the grandson of a Yankee Clipper captain with the painstaking analysis of the Berlin Ph.D. of 1900, and the erudition of the humanist. Each chapter begins with a literary quotation, some in French and Italian, several from Goethe, and one from Hans Sachs, the Meistersinger. One, from Sir Thomas More, Cady has applied to himself, in pride and modesty: "They gather also peerles by the sea side, and Diamondes and Carbuncles vpon certein rockes; and yet they seke not for them; but by chaunce finding them they cutt and polish them". It was a great privilege to be his student, coworker, and friend.

REFERENCES

1. W. G. Cady, Piezoelectricity, McGraw-Hill, 1946.

1a. W. G. Cady, Revised Edition, Dover Publications, 1964

2. F. Pockels, Goettinger Abhandl. 39, (1894).
3. W. G. Cady, Sound **2**, 46 (1963).
4. J. Valasek, *Phys. Rev.* 17, 475 (1921).
5. J. Valasek, *Phys. Rev.* 19, 478 (1922).
6. C. B. Sawyer and C. H. Tower, *Phys. Rev.* 35, 269 (1930).
7. Hans Mueller, *Phys. Rev.* 47, 175 (1935).
8. Hans Jaffe, *Phys. Rev.* 51, 43 (1937).
9. W. P. Mason, *Phys. Rev.* 55, 775 (1939).
10. Ref. 7, p. 189.