A 2400 year history of pyroelectricity: from Ancient Greece to exploration of the solar system

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A 2400 year history of pyroelectricity: from Ancient Greece to exploration of the solar system

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Pyroelectricity was probably first observed by the Greeks more than 24 centuries ago. The philosopher Theophrastus wrote that lyngourion (most likely the mineral tourmaline) had the property of attracting straws and bits of wood. For two millennia the peculiar properties of tourmaline were more a part of mythology than of science. In the eighteenth century pyroelectric studies made a major contribution to the development of our understanding of electrostatics. In the nineteenth, research on pyroelectricity added to our knowledge of mineralogy, thermodynamics and crystal physics. Pyroelectricity gave birth to piezoelectricity in 1880, and to ferroelectricity in 1920. The field of pyroelectricity flourished in the twentieth century with many applications, particularly in infrared detection and thermal imaging. Pyroelectric sensors have been carried on many space missions and have contributed significantly to our astronomical knowledge. BCT/701

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GREEKS AND ROMANS, DARK AND MIDDLE AGES

The Greek philosopher Theophrastus, who lived in the fourth century BC, probably wrote the earliest description of the pyroelectric effect, as exhibited by the mineral tourmaline (Fig. 1).[1] He described a stone called *lyngourion* that had the property of attracting straw and bits of wood. Theophrastus had thus observed the effects of electrostatic charges due to temperature changes of a pyroelectric material. A contemporary example is illustrated in a photograph in the classic book 'Piezoelectricity', by Walter Guyton Cady.[2] The photograph shows an accumulation of dust particles on tourmaline crystals that had been stored in a display case for several years. Although our present scientific interests concern the powers of attraction of *lyngourion*, Theophrastus and subsequent authors in the following two millennia were far more interested in the origin of the stone and its possible therapeutic properties. Theophrastus proposed that *lyngourion* was formed from the urine of an animal called a lynx. This was not the cat known today, but a doglike animal.

About 300 years later, Pliny the Elder, a Roman historian of the first century AD, repeated the story, giving the stone a Latin name, *lyncurium*.[3] More than 35 further works mention *lyncurium*, largely repeating the accounts of Theophrastus and Pliny with some embellishments. These works and authors include the Greek geographer and historian Strabo (*c.* 7BC);[4] a collection of Greek manuscripts called the 'Alexandrine lapidaries' (AD227–400);[5] Epiphanius, Bishop of Salamis on Cyprus (*c.* AD400);[6] the Spanish historian Isidore of Seville (*c.* AD600);[7] and Marbodus, Bishop of Rennes in France (*c.* AD1100).[8] An especially graphic description of the origin of *lyncurium* and its medicinal properties is given by Dioscorides, a first century AD Greek herbalist: 'But that [urine] of the Lynx, which is called Lyncurium, is thought as soone as it is pist out, to grow into a stone, wherefore it hath but a foolish report. For it is this that is called by somme, Succinum pterygophoron [because it drawes feathers to it], which being dranck with water is good for the stomach & for a belly that is troubled with a flux.'[9]

One of the most beautiful of the ancient books on natural history is the 'Hortus sanitatis major', the 'Garden of health', which describes the medicinal and therapeutic values of many plants, animals and minerals.[10] It was probably written by Johann Wonnecke of Caub in the fifteenth century and was published in Latin, German, French, Dutch and Italian editions. *Lyncurium* is described in several chapters, and a page containing an illustration of the origin of the stone according to Theophrastus is shown in Fig. 2.

EIGHTEENTH CENTURY

Two thousand years after Theophrastus, the unusual physical properties of tourmaline were reintroduced into Europe

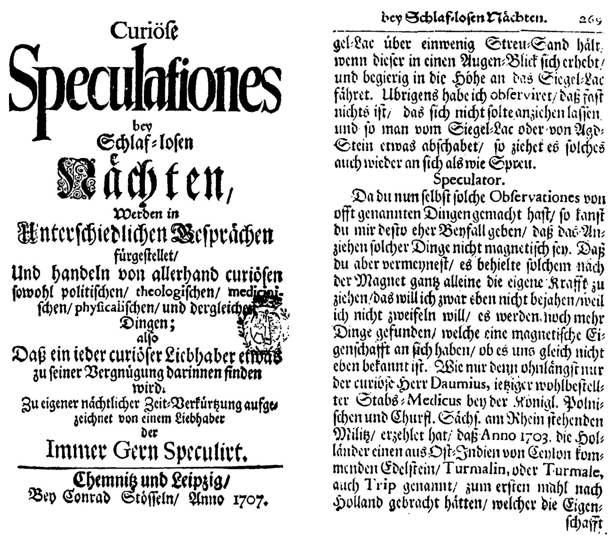
καὶ τὸ λυγγούριον* καὶ γὰρ ἐκ τούτου γλύφεται τὰ σφραγίδια καὶ ἔστι στερεωτάτη καθάπερ λίθος. ἕλκει γὰρ ὥσπερ τὸ ἤλεκτρον, οἱ δέ φασιν οὐ μόνον κάρφη καὶ ξύλον ἀλλὰ καὶ χαλκὸν καὶ σίδηρον ἐὰν ᾖ λεπτός, ὥσπερ καὶ Διοκλῆς ἔλεγεν. ἔστι δὲ διαφανές τε σφόδρα καὶ ψυχρόν.

"... remarkable in its powers, and so is the lyngourion, for seals are cut from this too, and it is very hard, like real stone. It has the power of attraction, just as amber has, and some say that it not only attracts straws and bits of wood, but also copper and iron, if the pieces are thin, as Diokles used to explain. It is cold and very transparent, and ..."

Theophrastus, *On Stones*
C. 315 BC

1 Quotation from Theophrastus[1]

2 Mythological origin of *lyncurium* according to Theophrastus,[10] with 'lynx' at lower right


Curiöse
Speculationes
bey
Schlaf-losen
Nächten,
Werden in
Unterschiedlichen Gesprächen
fürgestellet/
Und handeln von allerhand curiösen
sowohl politischen/ theologischen/ medicini-
schen/ physicalischen/ und dergleichen
Dingen;
also
Daß ein ieder curiöser Liebhaber etwas
zu seiner Vergnügung darinnen finden
wird.
Zu eigener nächtlicher Zeit-Verkürtzung aufge-
zeichnet von einem Liebhaber
der
Immer Gern Speculirt.
Chemnitz und Leipzig/
Bey Conrad Stösseln/ Anno 1707.

bey Schlaf-losen Nächten. 269

gel-Lac über einwenig Streu-Sand hält, wenn dieser in einen Augen-Blick sich erhebt/ und begierig in die Höhe an das Siegel-Lac fähret. Ubrigens habe ich observiret/ daß fast nichts ist/ das sich nicht solte anziehen lassen und so man vom Siegel-Lac oder von Agd-Stein etwas abschabet/ so ziehet es solches auch wieder an sich als wie Spreu.

Speculator.

Da du nun selbst solche Observationes von offt genannten Dingen gemacht hast/ so kanst du mir desto eher Beyfall geben/ daß das Anziehen solcher Dinge nicht magnetisch sey. Daß du aber vermeynest/ es behielte solchem nach der Magnet gantz alleine die eigene Krafft zu ziehen/ das will ich zwar eben nicht bejahen/ weil ich nicht zweifeln will/ es werden noch mehr Dinge gefunden/ welche eine magnetische Eigenschafft an sich haben/ ob es uns gleich nicht eben bekannt ist. Wie mir denn ohnlängst nur der curiöse Herr Daumius, ietziger wohlbestellter Stabs-Medicus bey der Königl. Polnischen und Churfl. Sächs. am Rhein stehenden Militz/ erzehlet hat/ daß Anno 1703. die Holländer einen aus Ost-Indien von Ceylon kommenden Edelstein/ Turmalin, oder Turmale, auch Trip genannt/ zum ersten mahl nach Holland gebracht hätten/ welcher die Eigen-
schafft

3 Pages from 'Curiöse Speculationes bey Schlaflosen Nächten'[11]

through the publication in 1707 of a book entitled 'Curiöse Speculationes bey Schlaflosen Nächten' ('Curious speculations during sleepless nights').[11] The author of the book, Johann Georg Schmidt, using the pen name *Immer Gern Speculirt* ('Always Gladly Speculating'), wrote a series of 48 dialogues, one of which contained a section describing hard and glassy bodies which were not magnetic (Fig. 3). An excellent description of the pyroelectric effect in tourmaline is given in this passage:

> The ingenious Dr Daumius, chief physician to the Polish and Saxon troops on the Rhine, told me, that, in the year 1703, the Dutch first brought from Ceylon in the East Indies a precious stone called tourmaline, turmale, or trip, which had the property of not only attracting the ashes from the warm or burning coals, as the magnet does iron, but also repelling them again. This sight was very amusing, for as soon as a small quantity of ashes leaped upon it, they appeared to be endeavouring to writhe themselves by force into the stone. Soon a few of the ashes jumped from it again, as if to leap to the tourmaline again. For this reason, it was called the ash-drawer by the Dutch. The colour of it was an orange-red heightened by a fire colour. When the turf coals were cold, the tourmaline did not produce these effects, and it required no care like the magnet ... I have considered whether it would not attract and repel the ashes of other burning coals as well as those of turf; and I have no doubt, that, if heated, it would attract other things besides ashes.

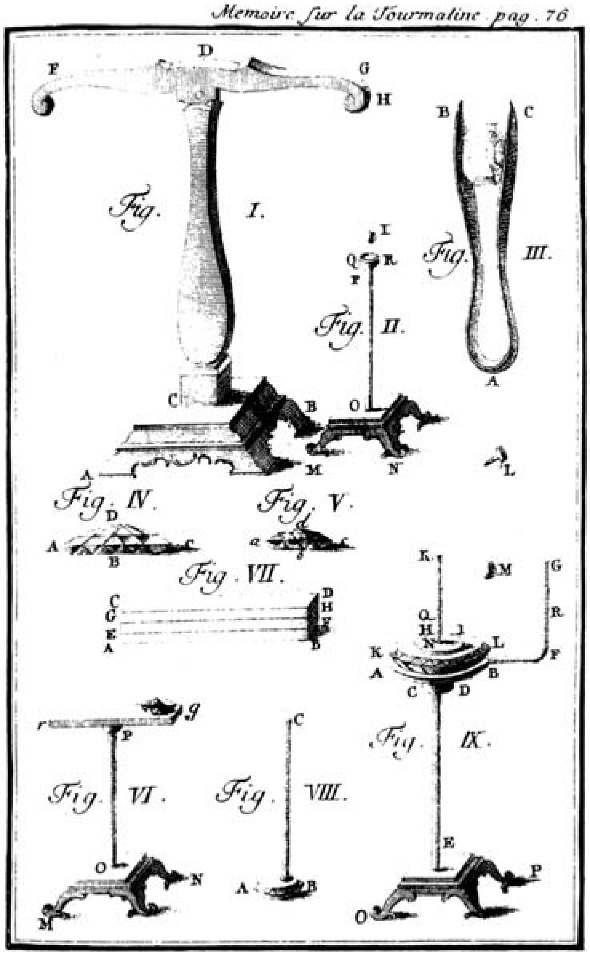
The first description of pyroelectricity in a scientific journal was by a physician and chemist, Louis Lemery, who exhibited a tourmaline crystal before the Academy of Sciences of Paris in 1717.[12] The naturalist Carl von Linné (Linnaeus) was the first person to relate the pyroelectric property of tourmaline to electricity. He called the mineral *lapis electricus*.[13] The first serious scientific study of the electrical properties of tourmaline was presented to the Royal Academy of Sciences in Berlin by Dr Franz Ulrich Theodor Aepinus in 1756.[14] His major observations were that tourmaline became electrified by being warmed (rather than by friction which was the common method in use at the time), and that the crystal acquired opposite electric charges on two opposing faces. Aepinus' observations strongly supported Benjamin Franklin's theory of positive and negative electricity, against the strong and weak electricity theory of Abbé Nollet. Figure 4 is an illustration from a publication by Aepinus.[14]

The usefulness of this new way of generating electric charges and its relevance to the rapidly developing understanding of electricity and magnetism induced many others to experiment on tourmaline, including Johann Karl Wilcke,[15] Benjamin Wilson,[16] Joseph Priestley,[17] John Canton[18] and Torben Bergman.[19] Additional references to papers by Wilcke, Wilson, Canton and Bergman are given in Ref. 20. An elaborate drawing of the apparatus of Bergman is shown in Fig. 5.[19] Canton was apparently the first person to observe that cooling of tourmaline caused its electrical polarity to be the reverse of that found on heating. He also devised a very novel experiment for demonstrating that the quantities of positive and negative charge were equal. He connected a metal cup filled with boiling water to a pith ball electroscope. A tourmaline crystal was dropped into the water and the electroscope showed no sign of electric charge, either then or during subsequent cooling of the water. This demonstrated that the absolute quantitites of positive and negative charge produced on the crystal were equal and were neutralised in the water.

NINETEENTH CENTURY

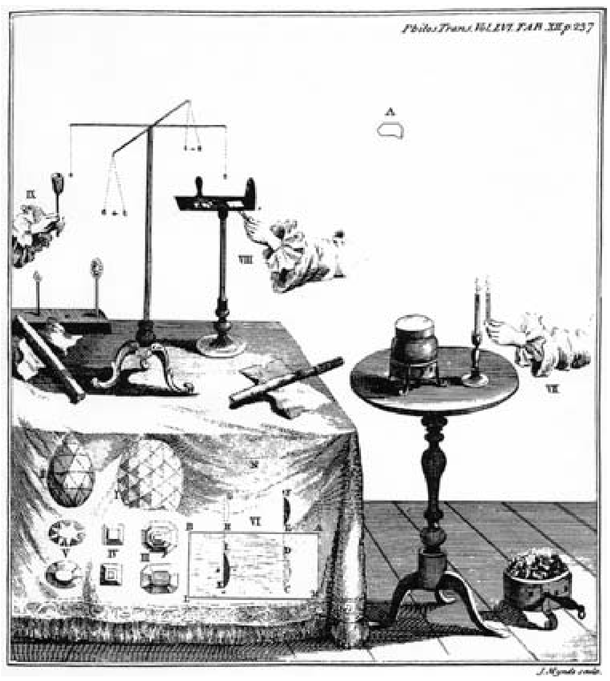
During the nineteenth century, research in pyroelectricity began to become more quantitative. As electrical measuring techniques of greater sophistication were developed, these were soon applied to pyroelectric studies.

David Brewster, famous for his work in optics, was the first author to use the term 'pyroelectricity'. It appeared in his 1824 paper entitled 'Observations on the pyro-electricity of minerals'.[21] One of the materials studied by Brewster

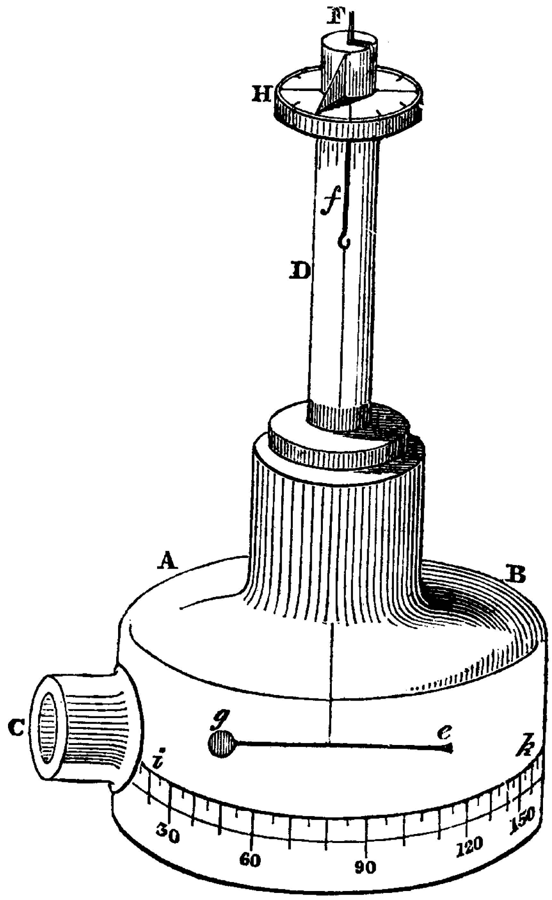


4 Experimental apparatus of Aepinus[14]

was the 'tartrate of soda and potash' – Rochelle salt – which was the material in which Valasek discovered ferroelectricity almost exactly a century later.[22] Quantitative electrometers for charge measurement were developed by A. C. Becquerel,[23] James D. Forbes[24]and Wilhelm Gottlieb



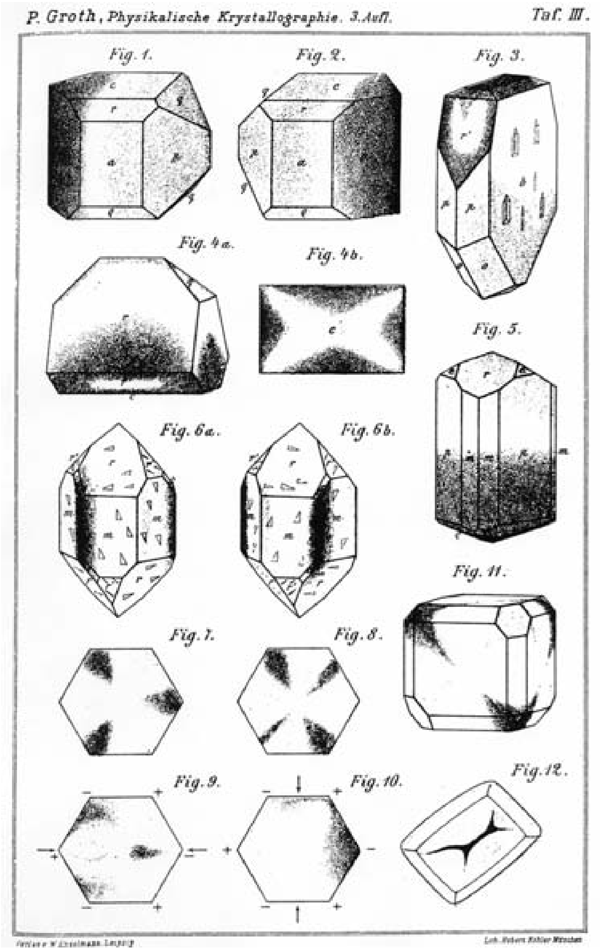
5 Experimental apparatus of Bergman[19]



6 Electroscope of Forbes[24]

Hankel.[25] Complete references to the papers written by Hankel are again given in Ref. 20. A drawing of the electroscope developed by Forbes is shown in Fig. 6. Hankel was one of the most prolific writers of all time on pyroelectricity, and published more than 30 very lengthy papers between 1839 and 1899.

Jean-Mothée Gaugain made the first precise measurements of pyroelectric charges in 1859.[26] He reached some important conclusions: first, that the total quantity of electricity produced by a crystal of tourmaline depends uniquely upon the limits within which its temperature is varied; second, that within the same temperature limits, the quantity of electricity produced during heating is the same as that produced during cooling, but with the signs of the charges reversed; and third, that the quantity of charge produced is proportional to the cross-sectional area of the crystal and is independent of its length. The first major theoretical treatment of pyroelectricity was published by William Thomson, Lord Kelvin, in 1878.[27] He was also the first person to predict the electrocaloric effect, the converse effect of pyroelectricity. A much used technique for determining the charge distribution on a crystal was developed by Kundt in 1883.[28] A mixture of red lead oxide and sulphur was dusted onto the crystal. The lead oxide adhered to the negative parts of the crystal and the sulphur to the positive parts. Figure 7 illustrates some typical results.[29] Jacques and Pierre Curie speculated that the electrical effects due to non-uniform heating of quartz crystals might be caused by pressure, which led to their discovery of piezoelectricity in 1880.[30] Woldemar Voigt, professor of physics at the University of Göttingen from 1883 to 1919, established an outstanding school of crystallography, thermodynamics and crystal physics. Many of the publications emanating from his school are described in his 'Lehrbuch der Kristalphysik'.[31]

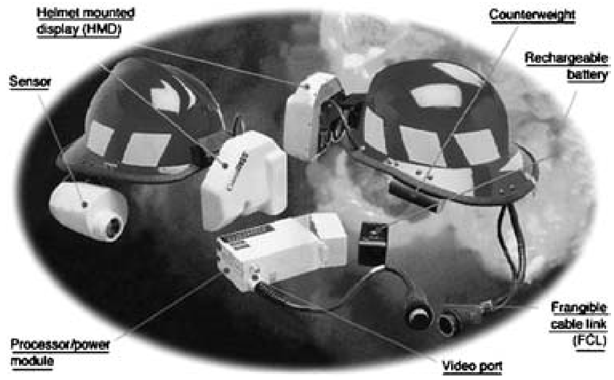


7 Kundt powder patterns:[29] materials shown are *d*-tartaric acid (Fig. 1), *l*-tartaric acid (Fig. 2), calamine (Fig. 3), struvite (Fig. 4*a*,*b*), tourmaline (Fig. 5), left and right handed quartz (Fig. 6*a* and *b* respectively), quartz plates (Figs. 7–10), boracite (Fig. 11), topaz plate (Fig. 12)

During the latter part of the nineteenth century and the early decades of the twentieth, seven Nobel laureates published papers on pyroelectricity. They are, of course, much better known for their research in other fields. Their names, the fields in which they received their Nobel prizes and details of their publications on pyroelectricity are given in Table 1.

TWENTIETH CENTURY

Few important papers on pyroelectricity were published in the first two decades of the twentieth century. Joseph Valasek studied the properties of Rochelle salt and, in 1920, discovered ferroelectricity.[22] Interest in pyroelectricity for a while then virtually vanished.



8 Pyroelectric IR imager in firefighter's helmet (courtesy UK Defence Evaluation and Research Agency, 1996)

In 1938, Yeou Ta published a paper that initiated the great growth in the field that continues today.[32] Ta, a chemist at the Sorbonne in Paris, proposed that tourmaline crystals could be used as infrared (IR) sensors in spectroscopy. In 1942, Sivian obtained a US patent for 'Energy translation utilizing pyroelectricity',[33] but there was little research on pyroelectric IR detectors over the next 15 years, and much of what there was is shrouded in classified documents, many of which are still not available. A small programme on pyroelectric IR detection was conducted at the Admiralty Research Laboratory in the UK in 1939 and 1940.[34] Matossi experimented on tourmaline detectors at the University of Graz in Austria during the Second World War.[35] No information has yet been released on IR detector research in the USA during that war. A report was published by Burns at the Chicago Midway Laboratories of the University of Chicago on a 'thermal image tube' in 1956,[36] and an MSc thesis on the use of $BaTiO_3$ as an IR detector was produced by Francis in 1957 at the Illinois Institute of Technology.[37] However, these latter two studies went largely unnoticed.

In 1962, Cooper made the first detailed analysis of the behaviour of a fast IR detector and conducted experiments using $BaTiO_3$.[38–40] In the same year, Lang proposed the use of pyroelectric devices for measuring temperature changes as small as 0·2 μK.[41] An explosive growth in theoretical studies, basic measurements and applications began, culminating in a total of more than 8500 publications during the period 1960–2003 (references to most of these publications may be found in Refs. 42 and 43). A description of accomplishments in this field in the past 40 years is beyond the scope of this paper. However, two areas will be mentioned which illustrate the potential of pyroelectricity.

In 1965, Hadni proposed the use of pyroelectric elements for thermal imaging.[44] Although early interest was in military and security applications, thermal television devices have had a significant impact in non-security areas. As an example, a thermal imaging sensor has been built into helmets worn by firefighters that enables them to see

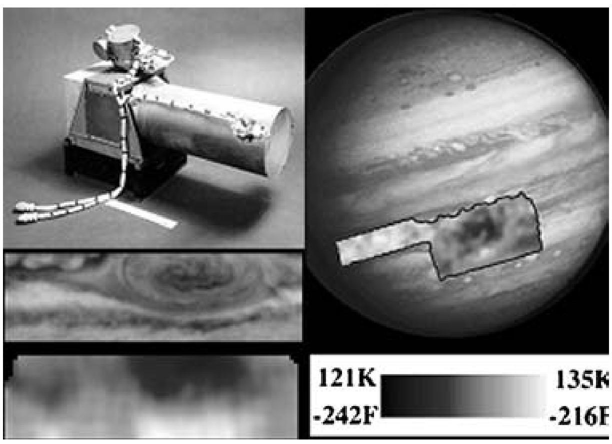
Table 1 Nobel laureates who have published on pyroelectricity

Laureate	Nobel prize	Work on pyroelectricity
Wilhelm Röntgen	Physics, 1901	Pyro- and piezoelectric investigations (1914)
Pierre Curie	Physics, 1903	Many papers on quartz and tourmaline (1880–1908)
Gabriel Lippman	Physics, 1908	Principles of conservation of electricity (theory of electrocaloric effect) (1881)
H. Kammerlingh Onnes	Physics, 1913	Piezoelectric and pyroelectric properties of quartz at low temperatures down to liquid hydrogen (1913)
Erwin Schrödinger	Physics, 1933	Kinetics of dielectrics: melting point, pyro- and piezoelectricity (1912)
Archer J. P. Martin	Chemistry, 1952	New method for detecting pyroelectricity (1931)
Max Born	Physics, 1954	Quantum theory of pyroelectricity (1945)

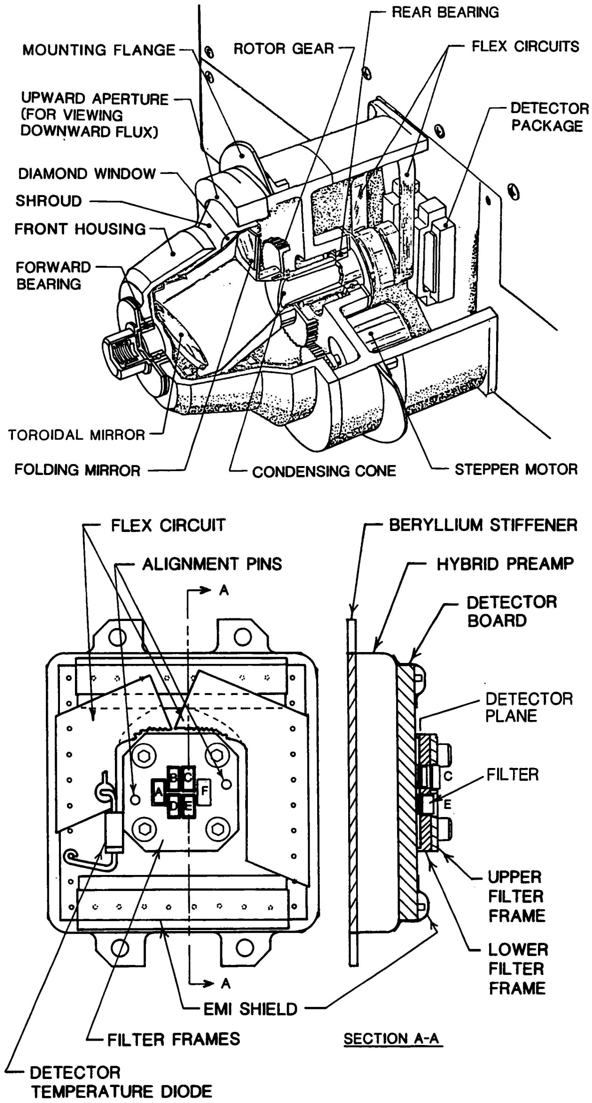
9 High resolution pyroelectric images: 256 × 128 pixels (above), 384 × 288 pixels (below) (courtesy UK Defence Evaluation and Research Agency, 1998)

through smoke and dust to locate the sources of fires and possible victims. An illustration of the helmet is shown in Fig. 8. Some of the highest resolution pyroelectric imaging devices have been developed at the UK Defence Evaluation and Research Agency. A 256 × 128 pixel image and a 384 × 288 pixel image are shown in Fig. 9.

Pyroelectric devices have been used for applications in space beginning with the vertical temperature profile radiometer launched into an earth orbit on the ITOS-D spacecraft in 1972.[45] One of the most recent space applications was in the Galileo mission which was launched on 18 October 1989. Included in its instrumentation was a photopolarimeter-radiometer used to determine thermal radiation on Jupiter and its moons.[46] The temperature distribution around the Great Red Spot of Jupiter is shown in Fig. 10. A probe carrying the net flux radiometer (NFR) was released into the atmosphere of Jupiter on 13 July 1995.[47] This device measured the vertical distribution of net flux of solar energy and planetary emission in order to help



10 Galileo photopolarimeter (upper left) and pyroelectric images of Great Red Spot of Jupiter[46] (courtesy NASA: see galileo.jpl.nasa.gov/images/jupiter/ppr.html)



11 Detector assembly of Galileo probe net flux radiometer:[47] optical head (above) and detector/hybrid assembly (below)

determine the chemical composition and structure of the Jovian atmosphere. The optical head and the detector/hybrid assembly of the NFR are shown in Fig. 11.

SUMMARY

In the eighteenth century, pyroelectricity emerged from two millennia of fable and myth into early studies of electricity, mineralogy, thermodynamics and crystal physics. It gave birth to piezoelectricity and ferroelectricity and has given rise to a large body of scientific knowledge and a host of applications. It continues to be a vibrant and active field of research today.

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