On a new method of detecting pyro-electricity.

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INTRODUCTION.—Pyro-electricity has been investigated by various methods. Sir David Brewster[1] heated his crystals and brought them into contact with small, very light, insulating particles. If these adhered, the presence of pyro-electricity in the crystal was inferred. He also used a very delicately suspended brass needle. Being a conductor it was attracted to a charged crystal when this was brought near to it. Hankel[2] placed the crystal under investigation in a small bath of copper or iron filings, which was then put into a hot-air oven. The filings did not entirely cover the whole crystal, but one corner, edge, or face, whichever was required, was left exposed. A very small platinum sphere connected to an electrometer was then brought near to the exposed portion. The charge induced on the sphere was taken as a measure of the charge developed at the particular spot on the crystal opposite the platinum sphere. Gaugain[3] attempted to make quantitative measurements by placing on the charged crystal a small hemispherical brass block connected to an electrometer which flicked and discharged itself whenever the potential rose to a certain value. The number of discharges occurring during the cooling of the crystal measured the total charge developed. Kundt[4] sprinkled a composite powder of two differently coloured, and oppositely charged constituents, over the crystal. The separation of the coloured powders and their position on the crystal indicated the presence and distribution of pyro-electricity. More recently, Hettich and Schleede[5] have developed a probe method. A small platinum point supported by an insulating handle is gently brought into contact with different

[1] D. Brewster, Edinburgh Journ. Sci., 1824, vol. 1, p. 208.
[2] W. G. Hankel, Abhandl. K. Sächs. Gesell. Wiss., 1859, vol. 4, p. 149.
[3] F. M. Gaugain, Compt. Rend. Acad. Sci. Paris, 1856, vol. 43, p. 916.
[4] A. Kundt, Sitzungsber. Akad. Wiss. Berlin, 1883, p. 421.
[5] A. Hettich and A. Schleede, Zeits. Physik, 1928, vol. 50, p. 249.

parts of the cooling crystal, and the charge induced on the platinum point is amplified and recorded by a galvanometer, the whole arrangement being very sensitive because of the use of modern electrometer-valves and valve-amplifiers. Meissner[1] has also investigated powdered crystals by placing them in a shallow layer between two plates a centimetre or so apart maintained at a difference of potential of about 8,000 volts. On heating and tapping the powder, the crystals, if pyro-electric, orientate themselves, so that on cooling a strong charge is induced on one of the plates if it is insulated and the other is earthed. The ice crystals which develop on a crystal hung in moist air after it has been cooled in liquid air may also be used to detect and investigate pyro-electricity.[2]

The method presented here is simple and probably as sensitive as any used previously. It has two advantages because low temperatures are used; the crystals are not decomposed and the insulation of all crystals which are not metallic is increased by cooling. Further, the experimental conditions are more definite than is usually the case, in that the crystal is at the same temperature at every point during the experiment.

The importance of pyro-electricity is the help it gives in the determination of space-groups. Pyro-electricity is of two kinds, 'true' and 'false'. 'False' pyro-electricity is the piezo-electric charge developed by the thermal deformation consequent on heating or cooling, and occurs in any crystal lacking a centre of symmetry. 'True' pyro-electricity is a theoretical conception which could only arise in crystals possessing a single polar axis, but in fact it has never been unambiguously demonstrated. Since in this experiment the crystal arrives at the same temperature throughout, the deformation may be considered homogeneous and only those crystals possessing a single polar axis can show any effect.

Experimental Method.—The apparatus (fig. 1) consists of a Dewar flask with an unsilvered strip, containing liquid air, in which is immersed a metal plate *A* supported on a glass rod which is pivoted at *C*. By employing a sufficiently long handle *F*, it is possible to move *A* a very small distance with certainty. Opposite the plate *A*, the crystal to be tested, *B*, is suspended by a glass fibre *D*, to which it is attached by a loop of cotton or, in the case of very small crystals, by Kodak mounting paste. At the other end, the glass fibre is carried

[1] A. Meissner, Die Naturwissenschaften, 1929, vol. 17, p. 25.

[2] M. E. Maurice, Proc. Cambridge Phil. Soc., 1930, vol. 26, p. 491.

by a hook attached to a rotatable head (a cork carrying a glass rod), so that the orientation of the crystal to the plate may be varied.

The procedure is as follows. The crystal, mounted as described, is lowered gently into the liquid air, and, after ebullition has ceased,

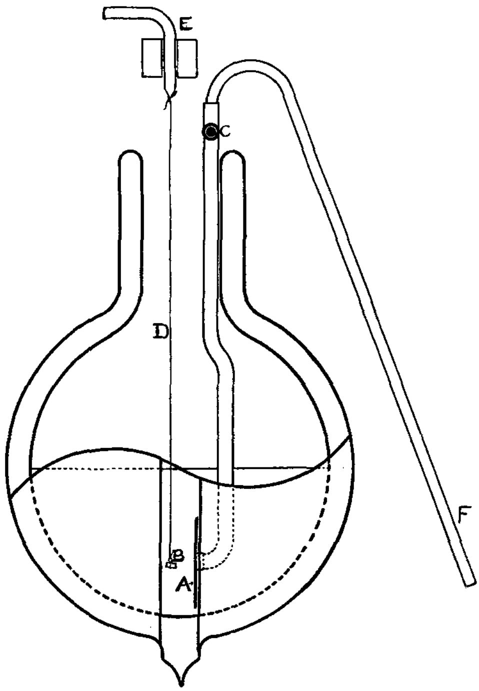

FIG. 1. Dewar flask with arrangement for detecting pyro-electricity. (The lower half of the figure represents an actual side-view of the apparatus whilst the part above the wavy line is a sectional view.)

the metal plate is moved towards the crystal very slowly. A pyro-electric crystal is attracted towards the plate by the induced charge, and clings to the plate as the latter is withdrawn. Tourmaline and rochelle salt adhere so vigorously that it is difficult or impossible to shake them off.

The position of the electric axis may in general be found by rotating the crystal and finding which part adheres most strongly: this is the end of the electric axis.

Because of the low temperature the rate of loss of charge is generally very slow (tourmaline retains much of its charge after half an hour), and observations may be repeated many times before it becomes necessary to withdraw the crystal and allow it to warm up again.

Crystals of more or less cubical shape, with sides from one centimetre to one millimetre, may conveniently be employed, or needles or plates 0·1 mm. thick, provided the electric axis be parallel to the length of the needle or to the plane of the plate.

Results.—The investigation was started in order to test thomsonite, nepheline, and dioptase for pyro-electricity. All of these showed the effect, six crystals of dioptase being investigated. It is remarkable that in text-books dioptase is usually given as the typical member of the rhombohedral class of the trigonal system, and should therefore possess a centre of symmetry. It appears from this work that dioptase cannot belong to the same class as phenakite, willemite, dolomite, pyrosmalite, and ilmenite, none of which showed any trace of pyro-electricity when tested by this method.

The statement about dioptase is not new, as Hankel[1] investigated eight crystals and found three of them negative at both ends on cooling, and positive in the middle, whilst the other five were positive at one end and negative at the other.

Boracite, struvite, axinite, prehnite, scolecite, and asparagine all showed a positive effect. Among crystals possessing more than one electric axis, quartz, cinnabar, epsomite, barium nitrate, and zincblende were tried and showed no effect. It is to be noted that boracite is not cubic at ordinary temperatures.

In suggesting a new method of investigating a phenomenon it is desirable to compare it with other methods. The powder method of Kundt is suitable only for substances which have a fairly strong effect and occur as crystals larger than 3 mm. cube. The electrometer methods of Hankel and Gaugain can be applied only to fairly large crystals; and although the writer has no experience of Meissner's probe method, he considers it of doubtful value with crystals less than 3 mm. cube. Meissner's orientation method is suitable for fine powders, but the apparatus is relatively complicated. The piezoelectric method of Giebe and Scheibe,[2] in which small crystal grains are made to execute very high frequency mechanical vibrations by means of a valve-oscillator, is especially applicable to small crystals

[1] W. G. Hankel, Abhandl. K. Sächs. Gesell. Wiss., 1883, vol. 12, p. 549.
[2] E. Giebe and A. Scheibe, Zeits. Physik, 1925, vol. 33, p. 760.

(less than 3 mm. cube), but a weak effect is very difficult to detect. The method presented here is generally unable to detect any effect if more than one electric axis be present. This limitation is not present in some of the other methods mentioned, and the present method and that of Giebe and Scheibe should be regarded as complementary, and should both be employed in detecting the absence of a centre of symmetry.

Summary.—1. A new experimental method of detecting pyro-electricity is given, which depends on the attraction between a charged crystal and a metallic conductor, the charge being developed by cooling the crystal in liquid air.

2. Results for a number of crystals are given, attention being drawn to dioptase, which although placed in a centro-symmetrical class, yet shows definite pyro-electricity.

3. A comparison is made between this and other methods.

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