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The Pyroelectric Behaviour of Colemanite

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A new, highly sensitive and convenient technique for detecting pyroelectricity in crystals has been used to study the pyroelectric behaviour of colemanite over the temperature range from that of liquid helium to +100° C. Colemanite exhibits only one phase transition over this range, at −6° C. Above this temperature colemanite is not pyroelectric, while below, it is pyroelectric and ferroelectric.

Introduction

Studies of electrical breakdown paths by Davisson (1956) and X-ray investigations by Christ (1953) seem to indicate that colemanite is centrosymmetrical from −195° C. to +150° C. though pyroelectric and piezoelectric tests suggest otherwise. Davisson found colemanite to be both pyroelectric and piezoelectric, that the curve of pyroelectric coefficient versus temperature goes through a high and narrow peak at −2·5° C., possesses an appreciable tail extending to low temperatures and a rapidly decreasing tail on the high-temperature side. Using a convenient and highly sensitive technique developed by the author (Chynoweth, 1956*a*), the pyroelectric behaviour of colemanite has been redetermined. The results are in substantial agreement with Davisson's pyroelectric measurements.

Principle of the pyroelectricity technique

The temperature of small crystals can be altered both appreciably and rapidly by subjecting them to fairly intense flashes of radiation from a suitable light source. During a flash, the temperature changes at the rate (dT/dt), which, in turn, causes the spontaneous polarization, P_s, if present, to change at the rate (dP_s/dt). This quantity is manifested as a current, i, in an external circuit, where

$$i = 2A(dP_s/dt) = 2A(dP_s/dT)_T(dT/dt)_T; \quad (1)$$

where $(dP_s/dT)_T$ is the pyroelectric coefficient at temperature T, and A is the electrode area. The factor (dT/dt) varies only slowly with the temperature except when C_p, the specific heat at constant stress, is changing rapidly, as at phase transitions or at low temperatures (Chynoweth, 1956*a*). Thus, changes in i with temperature reflect mainly changes in (dP_s/dT). Using a rotating chopper to modulate the light beam, the fluctuating temperature of the crystal gives rise to an alternating pyroelectric current.

Experimental details

The crystals of naturally occurring colemanite used for these experiments were supplied by Dr C. L. Christ. Thin slices could be cleaved from the parent crystals quite easily. One major face of the crystal, (010) (Christ, 1953), was grounded by cementing it with silver paste directly on to a metal block forming part of a cryostat, a good thermal contact being ensured thereby. A lead attached to a silver paste electrode on the opposite crystal face led to an amplifier of suitably high input impedance (10^6 ohms). The crystal was cooled to the temperature of liquid helium and then allowed to warm slowly to room temperature. A thermocouple attached to the metal block, indicating the crystal temperature, was fed into the Y input of an X–Y paper recorder. Using a chopper of equal light and dark intervals, the alternating pyroelectric current so produced was amplified and rectified and then fed on to the X input of the recorder. Thus, as the crystal was slowly warmed, the recorder traced out a curve of pyroelectric current versus, in effect, the crystal temperature. A tungsten projection lamp was used for the light source; the pyroelectric signal is independent of the spectral quality of the light, provided that selective absorption in the crystal–electrode unit is not too important. For display of the pyroelectric signal the output of the amplifier was applied also to an oscilloscope.

Results

Fig. 1(*a*) shows the pyroelectric current versus temperature from −250° C. up to 50° C. As Davisson found, the pyroelectric current goes through a high and sharp peak just below 0° C., while at lower temperatures the current remains low and shows little variation until below −150° C. Here, the current shows some increase with further lowering of the temperature and, after reaching a peak, drops sharply towards zero. This increase in i as the temperature drops is most likely a result of the temperature variation of the specific heat. At low temperatures, the fall in C_P will result in a higher value of (dT/dt), and hence of i also, if (dP_s/dT) is roughly constant. The actual magnitude of the current at the lowest temperatures is not too accurate because of distortions in the pulse shape; possibly these were caused by the thermal relaxation time of the crystal becoming com-

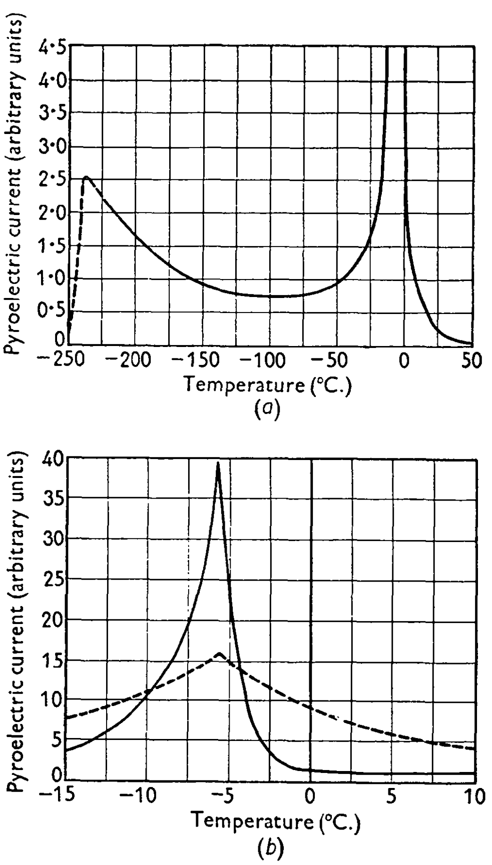

Fig. 1(*a*). The temperature dependence of the pyroelectric current in colemanite. For the broken portion of the curve, the temperatures were not known accurately. (*b*) The temperature dependence of the pyroelectric current in the neighborhood of the Curie point. The full line is for a crystal with a sharp transition, the broken line shows the behavior frequently encountered with poor-quality crystals. The two curves are normalized at −100° C.

parable to the duration of the light flash. The final rapid plunge of the current towards zero requires further investigation, though it is certainly connected with the way in which the fraction $(dP/dT)/C_P$ behaves as the temperature approaches absolute zero.

The peak in the pyroelectric current is shown in detail in Fig. 1(*b*) by the full line. The peak occurs at about −6° C. and has a half-width of 3° C. These figures agree well with Davisson's footnote observations. A sharp peak in the pyroelectric signal indicates a discontinuity in the pyroelectric coefficient, the specific heat, or both. Certainly, it indicates the occurrence of a phase transition. On the high-temperature side of the peak the current drops very rapidly to a small value though there is a tail, as shown in Fig. 1(*a*), which persists in a steadily decreasing manner to higher temperatures. Even in good-quality single crystals of barium titanate such tails are frequently observed above the Curie point where the polarization, and hence the pyroelectric coefficient, should be zero (Chynoweth, 1956*b*). These tails may be explained by the presence of space-charge fields inside the crystal resulting in an induced polarization when the crystal is in the paraelectric state. Alternatively, strains present in the crystal may sometimes cause the transition temperature to be altered in parts of the crystal though prohibitive strains would be required to shift the transition temperature by 50° C. or more. Many colemanite crystals showed a much broader transition region; such a result is shown by the broken curve of Fig. 1(*b*), which was normalized to the previous example at −100° C. The peak is very much lower though it occurs at about the same temperature as did that of the crystal with the sharp transition. A sizeable tail persists on the high-temperature side to 100° C. or more. In all cases, however, the current appeared to approach zero if the temperature was made sufficiently high. It may be concluded, therefore, that at temperatures greater than about −5° C. an ideal single crystal of colemanite shows no pyroelectric effect. Below the transition temperature, a pyroelectric effect exists right down to liquid-helium temperature, and the crystal is therefore non-centrosymmetric in this range.

Before discussing the experimental results further it is necessary to consider briefly the way in which the pyroelectric signal is produced. The magnitude and direction of the current in the external circuit depends on the relative dispositions of the electrodes applied to the crystal, the parts of the crystal that are heated by the radiation, and the direction of the net spontaneous polarization vector. In the arrangement used for the colemanite studies radiation of W W.cm.$^{-2}$ struck the crystal and its electrodes in a direction normal to the electrodes. Consider unit electrode area and let P_x be the component of the spontaneous polarization in the direction perpendicular to the electrodes. There are two important cases to consider: (i) the radiation is absorbed incompletely though more or less uniformly throughout the crystal volume, and (ii) the radiation energy is entirely absorbed within the crystal and its electrodes, possibly in a narrow region close to the first electrode struck by the radiation.

(i) For the case of uniform heating we have

$$aWd = \varrho d C_p (dT/dt)\,,$$

where a is a constant representing the energy absorbed per cm. in the thickness direction, d is the crystal thickness, and ϱ is its density. Maintaining the radiation for a time δt produces a change δP_x in the spontaneous polarization, where

$$\delta P_x = (dP_x/dT)(dT/dt)\delta t = (dP_x/dT)aW\delta t/\varrho C_p\,.$$

Hence,

$$i = 2(dP_x/dt) = 2(dP_x/dT)aW/\varrho C_p\,,$$

and, in particular, the current is independent of the crystal thickness.

(ii) For the case of non-uniform heating, let l be the thickness of the layer near the crystal surface in which all the radiation is absorbed. Then we have

$$W = l\varrho C_p(dT/dt)_l\,,$$

provided that there is negligible heat flow out of the layer during the light pulse. This is a reasonable approximation since the thermal relaxation time for pyroelectric materials is usually of the order of seconds, which is to be compared with the duration of the light pulse, that is, milliseconds. The approximation may break down, however, at very low temperatures. Now the change δP_z produced in the layer is electrically equivalent to a change in the charge induced on the electrodes of $2\delta P_z l/d$. Thus, the expression for the pyroelectric current becomes

$$i = 2W(dP_z/dT)/\varrho C_p d$$

and, in particular, the current varies inversely as the crystal thickness. Extensive measurements (Chynoweth, 1956*a*) on barium titanate crystals with semitransparent evaporated electrodes in the normal direction showed that the current followed such a dependence on the crystal thickness. From this it is concluded that in these crystals (which are more or less transparent in the spectral range corresponding to the radiation from the tungsten lamp), as well as for other crystals under similar conditions, the amount of energy absorbed is independent of the crystal thickness. This suggests that most of the absorption occurs at the electrode with consequent heating of the surface layers. Certainly this is likely to be the case when silver paste electrodes are used.

The pyroelectric coefficient, $p_{2z} = (dP_z/dT)$, used in the above expressions is, in practice, the secondary pyroelectric coefficient which occurs when the crystal is subjected to uniform heating at constant stress. (The primary pyroelectric coefficient occurs at constant strain.) It was concluded above that the incident energy is absorbed in a thin layer. Thus, though the heating can be regarded as uniform within the layer, a growing temperature gradient, (dT/dx), is produced between the layer and the rest of the crystal. This temperature gradient can give rise to a tertiary pyroelectric effect, p_{3z}, the magnitude of which depends on that of the temperature gradient. Thus, the total pyroelectric current during the light pulse has the form

$$i = Ap_{2z} \pm Bp_{3z}t\,,$$

where A and B are constants. Clearly the secondary and tertiary pyroelectric effects can be separated by inspection of the shape of the current pulse displayed on the oscilloscope. If the effect of non-uniform heating is negligible, the pulse shape is square; if the effect is important, the square pulse will have superimposed on it a linearly sloping portion. If only the tertiary effect occurs in a given crystal then the current will increase linearly from zero during the pulse.

A photograph of the current waveform taken at a few degrees below the transition temperature is shown in Fig. 2. An asymmetrical chopper was used, the shorter interval corresponding to the light pulse being a few milliseconds in duration. The waveform was very similar over the whole of the pyroelectric range except at temperatures approaching that of liquid helium. The fairly slow rise in the current corresponds to the time taken for the chopper edge to sweep through the light beam. The current thus grows as rapidly as the incident energy to a constant value; it was verified that the very slight drop-off during the light pulse was completely explained by the low-frequency cut-off of the amplifier. Hence, the pyroelectric signals are interpreted as being caused by the secondary type of pyroelectric effect and, therefore, the crystal is classed as a true pyroelectric.

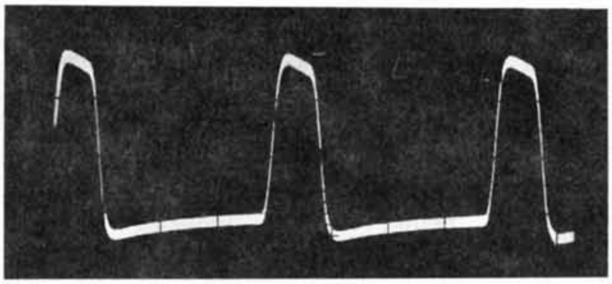

Fig. 2. Photograph of the pyroelectric current waveform at a temperature below the phase transition.

In general, though no voltage is applied to the crystal, photovoltaic currents are possible, in principle, because of local space charges present in the crystal. To be certain that the current signals obtained from the colemanite crystals were pyroelectric rather than photovoltaic in origin, some additional tests were made. Because colemanite is transparent, placing a filter in the light beam so as to absorb all the blue and ultra-violet radiation should reduce considerably any photovoltaic effect present (as this is usually strongest when a crystal is excited in its fundamental absorption band) while affecting to a negligible extent a pyroelectric effect (the filter reducing only slightly the total energy falling on the crystal). It was found that the filter produced only slight reduction in the current, and most of this drop could be accounted for by reflection losses. To be certain that the currents were not the result of carriers being liberated at impurities a d.c. measurement was made using a sensitive electrometer in the crystal circuit. The crystal was subjected to the light for a period long enough to allow it to reach thermal equilibrium. When $(dT/dt) = 0$, there was no measurable current. If a photovoltaic effect were present, a steady current should flow indefinitely. Furthermore, cutting off the light would cause a photovoltaic current to decay smoothly to zero without changing sign, whereas a pyroelectric current would actually reverse its sign (as (dT/dt) becomes negative) and then approach zero. The current reversal occurred when the light was cut off, thereby demonstrating conclusively that the currents were pyroelectric in origin.

In interpreting the results obtained with the pyroelectric technique it is necessary to consider the meaning of P_x, the component of the net spontaneous polarization in the direction perpendicular to the electrodes. The crystal under investigation may not be a single crystal; it may be comprised of a number of crystallites, the polarization axes of which are directed somewhat at random. However, though the value of P_x is smaller than it would be if all the polarization axes were aligned along the x axis in the same sense, it is highly unlikely that the net value of P_x is zero if the number of crystallites is not too large. This also applies to multi-domained single crystals. Because of the high sensitivity of the method, the loss in magnitude of P_x is generally not too serious. Usually, no difficulty was experienced in detecting the pyroelectric signals in colemanite crystals, even in those which were clearly not single crystals. In the case of a single crystal, P_x can be zero and it may be necessary to test the crystal along at least three different directions. This check was made on the colemanite crystals that showed a negligible pyroelectric effect above the transition temperature. The continued failure to obtain pyroelectric signals showed that the transition was not simply a change in the orientation of the polarization vector, but that the polarization, P_s, really did become zero.

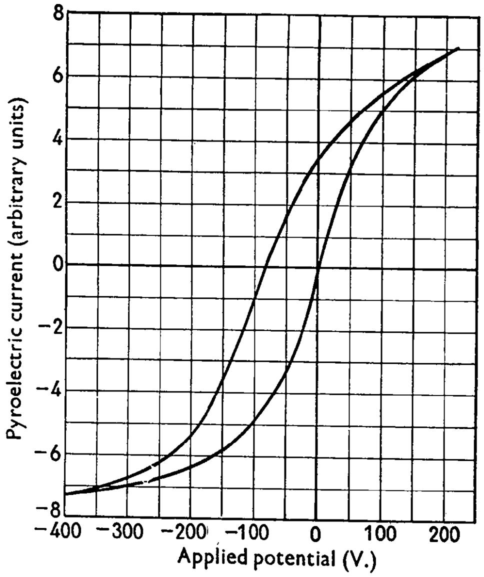

Fig. 3. Pyroelectric hysteresis loop at −50° C.

Below the transition temperature colemanite was found to be ferroelectric because the direction of the spontaneous polarization, and hence also that of the pyroelectric current, could be reversed by appropriate electric fields*. Fig. 3 shows a hysteresis loop obtained for the pyroelectric current at −50° C., the field being cycled completely in about 2 min. The loop is markedly biased, being similar in this respect to the loop observed in some other classes of ferroelectric crystals (Holden, Merz, Remeika & Matthias, 1956). At the widest part of the loop, the value obtained for the quasi-static coercive field was about 2500 V.cm.$^{-1}$. The coercive field varied slowly with the temperature except close to the transition temperature; in this region approaching the transition from below resulted in a rapid decrease in the coercive field with it reaching zero at the transition. The crystals available did not yield very satisfactory hysteresis loops when examined at 60 c.sec.$^{-1}$ and it was not possible to obtain a reliable value for P_s. Because the applied field can create in the crystal a space-charge field which remains when the external field is removed, the tests described above for differentiating between pyroelectric and photovoltaic effects were performed. They showed that photovoltaic currents were completely negligible compared with the pyroelectric currents.

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* It is understood that Dr G. Goldsmith of the R.C.A. Laboratories has found colemanite to be ferroelectric prior to this author's measurements.