Thermal Expansion in Silver Halides

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THE purpose of this letter is to call attention to some interesting data obtained by Strelkow[1] on the thermal expansion of the silver halides. Strelkow and his collaborators[1] have measured the thermal expansion of a large number of substances, including Bi, Zn, Cd, NaCl, AgCl, and AgBr, and find a rather striking anomalous expansion just below the melting points of these substances. The effects appear to be real pre-melting phenomena and not instrumental errors arising from creep.

The possibility of observing anomalous expansion in silver halides has been the subject of speculation by Mott and Gurney[2] and also by Seitz[3] who appear to be unacquainted with Strelkow's data. Accordingly, I present these data in a modified form in Fig. 1, in which I have plotted the logarithm of the anomalous increase in length as a function of the reciprocal of the absolute temperature. In this graph I have corrected Strelkow's data for the normal expansion of these solids by subtracting the change in length corresponding to an average expansion coefficient of 3.2×10^{-5}/°C for AgCl and 3.6×10^{-5}/°C for AgBr. These values are subject, however, to a certain amount of doubt. Nevertheless, the resultant points fall reasonably well on straight lines, suggesting the abnormal expansion arises from an activation process. The heats of activation derived from Fig. 1 are tabulated in Table I, where they are compared to the heats of activation

TABLE I. Heats of activation in cal./mole

	From expansion data	From conductivity data[a]
AgCl	7,100	12,500
AgBr	10,500	10,100

[a] Estimated by F. Seitz from the data of E. Koch and C. Wagner (Zeits. f. physik. Chemie **B38**, 295 (1937) on the conductivity of silver halides doped with lead halides.

determined from observations on the electrical conductivity of pure and doped salts.

In the case of AgBr, at least, the correlation is quite good and suggests that the anomalous expansion arises from the increase in the number of lattice defects which are responsible for the ionic conductivity. Since some doubt exists as to the nature of these defects (i.e., whether they are Frenkel or Schottky defects) it is of interest to ascertain whether the expansion data are capable of discriminating between the two possibilities.

Assuming a Frenkel mechanism and that the holes and interstitial Ag^+ atoms conduct equally, Seitz[3] has given the following relation for the fraction of defects in a AgBr lattice:

$$n/N=29e^{-5050/T}.$$

For $T=690$°K we obtain a concentration of 2 percent defect lattice sites. If we assume that the increase in volume on the formation of a hole and an interstitial Ag^+ ion is about 0.25 times the volume originally occupied by the Ag^+ ion, and take into account the radii of the Ag^+ and Br^- ions, then the estimated increase in volume of the lattice at $T=690$°K is about 0.2 percent. On the other hand, if we assume that the defects are pairs of equally mobile Schottky holes and that the volume on the formation of such a pair is about 0.70 of the volume originally occupied by the Ag^+ and Br^- ions, then the estimated increase in volume at $T=690$°K is 1.4 percent. If one of the pair of Schottky holes is much more mobile than the other, the estimated increase in volume at this temperature would be 2.8 percent. Since the observed increase in volume in silver bromide at $T=690$°K is actually 2.9 percent, Strelkow's data would seem to favor the last model as the mechanism of conductivity in AgBr. This conclusion

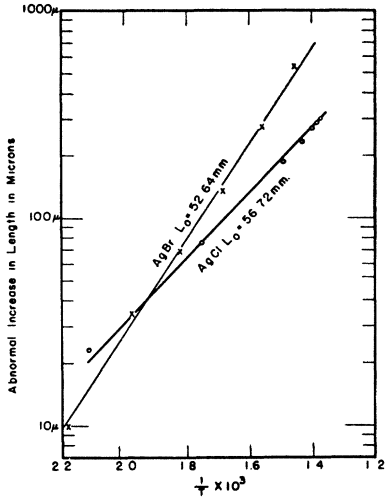

FIG. 1. Anomalous thermal expansion in AgBr and AgCl.

is not in conflict with the data of Breckenridge,[4] and recently arguments supporting this mechanism have been advanced by Mitchell.[5]

Unfortunately, the situation does not seem to be so clear cut in the case of AgCl. The heats of activation estimated from the expansion data and the conductivity data are in poor agreement. However, the expansion effect is much smaller in AgCl, and it is difficult to obtain a good estimate of the heat of activation from Strelkow's data. In fact there is some indication that the heat of activation is considerably higher just below the melting point of AgCl than the value given in Table I, but the data are insufficient to permit a definite statement on this point. The conclusion reached in the case of AgBr, however, suggests that further experiments on AgCl would cast considerable light on the mechanism of the conductivity in this case also.

[1] P. G. Strelkow, Physik. Zeits. Sowjetunion **12**, 77–82 (1937).
[2] Mott and Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1948).
[3] F. Seitz, Phys. Rev. **56**, 1063 (1939).
[4] R. G. Breckenridge, Technical Report 26, Laboratory for Insulation Research, M.I.T.
[5] J. W. Mitchell, Phil. Mag. **40**, 667 (1949).

Causes of Abnormal Efficiencies in Scintillation Counters*

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IN the detection of beta- and gamma-rays with scintillation counters, numerous investigators have obtained efficiencies up to several times higher than those predicted theoretically.[1] The purpose of this note is to discuss some sources of these extra counts. Scattered gamma-rays, delayed pulses produced in the photo-multiplier tube or crystal, and multiple pulses from the amplifier when overloaded, have been suggested.[1]

For the Jordan-Bell amplifier[2] used with our counter, we observed a long second pulse to follow strong scintillation pulses, resulting in a sharp turn-up of the integral bias curve for small pulse heights (Fig. 1; the pulse height scale is a relative one, the smallest measured pulses being 10 volts high, to minimize the effect of any instability in the discrimination level). Tests with artificial pulses showed that these second pulses were due to overloading in the amplifier. When the detection of nearly all the

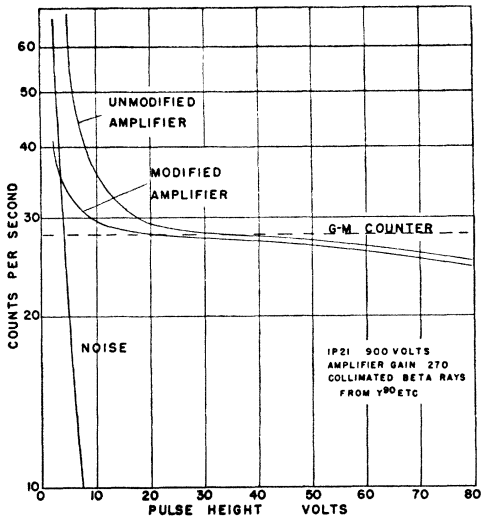

FIG. 1. The effect of spurious pulses on the low energy end of an integral bias curve.

Compton electrons produced in the crystal by gamma-rays is required, the range of energies of these electrons makes it essential that the amplifier be able to handle a wide range of pulse sizes.

When these second pulses had been eliminated by crystal diode clippers in the amplifier, the bias curve of pulses from an anthracene scintillation counter, illuminated by a well-collimated beam of beta-rays, still turned up sharply for pulse heights smaller than 10 volts, corresponding to 70-kev electrons (Fig. 1, noise rate subtracted). The correct beam strength shown was determined to within 1 percent with an end-window Geiger counter. An aluminum foil placed between the crystal and the photo-multiplier reduced the counting rate, at the lowest bias setting used, to less than 1 percent of that given by the crystal, showing that the extra counts were not due to beta-rays acting directly on the photo-multiplier. Similar results were obtained with anthracene purified by three independent methods[3] and with stilbene.

By introducing a variable deadtime it was shown that about half the extra pulses occurred within 200 microseconds of another pulse, and more small pulses were indeed observed on a scope during the 200 microseconds following large pulses than in an equal time 800 microseconds later. Pile-up of noise and signal pulses, which can lead to abnormal efficiencies, was not appreciable for the conditions used.

The crystal was removed and the same photo-multiplier illuminated by artificial flashes, 3 microseconds long and bright enough to give pulses larger than the largest ones from anthracene excited by Y^{90} beta-rays. At the minimum bias setting used the counting rate due to signal and noise together was equal, to within 1 percent, to the sum of the separate signal and noise rates. Hence under the conditions used, such light flashes produced no measurable secondary pulses in the photo-multiplier tube[4] or electronic equipment.

Except for the remote possibility that the much shorter flashes from anthracene, of about the same intensity, produce delayed pulses in the photo-multiplier, the extra pulses can only be delayed scintillations from phosphorescent decay in the anthracene.[5] The size of the extra pulses is compatible with their being produced by single electrons from the photo-multiplier cathode. That a weak, relatively long-period phosphorescence exists in anthracene and stilbene is demonstrated by removing a strong source from beside the scintillation counter. Counting continues for several seconds, while no such effect occurs with the photo-multiplier tube alone.

A much stronger long-period phosphorescence is exhibited by scheelite and artificial calcium tungstate crystals. By taking the counting rate at a sufficiently low bias, apparent efficiencies of several hundred percent can be obtained.

Because the delayed scintillations from anthracene extend over several hundred microseconds, we have usually found it impracticable to eliminate them by the use of an artificial deadtime. For incident gamma-rays of 2.5 Mev or less, they are apparently important only when electrons with energies less than about 70 kev must be measured. Projecting the straight part of gamma-ray integral bias curves (for organic crystals) back to zero pulse height has repeatedly given counting rates agreeing with the calculated rates to within 5 percent.

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** Now at the Chalk River Laboratory, National Research Council of Canada, Chalk River, Ontario, Canada.
[1] Rochester Conference on Scintillation and Crystal Counters (1948); R. Hofstadter, Phys. Rev. **75**, 796 (1949); G. J. Hine, Science **110**, 380 (1949).
[2] W. H. Jordan and P. R. Bell, Rev. Sci. Inst. **18**, 703 (1947).
[3] By Professor J. A. Irvine of M.I.T., by the Harshaw Chemical Company and by the Reilly Tar and Chemical Company.
[4] With high photo-multiplier voltages, false pulses from photo-multiplier tubes have been reported. Oak Ridge Symposium on Scintillation Counters (1949); AECU 583.
[5] Delayed pulses from anthracene excited by very high energy protons were reported by L. Wouters, Oak Ridge Symposium on Scintillation Counters (1949).