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 $3.2 \times 10^{-5}/°C$ for AgCl and $3.6 \times 10^{-5}/°C$ 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
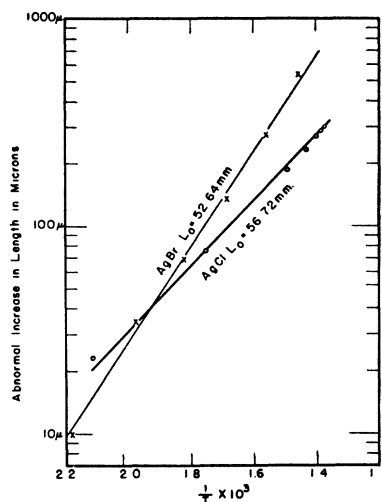

FIG. 1. Anomalous thermal expansion in AgBr and AgCl.

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