Lattice Defects in Silver Bromide

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AN anomalous specific heat of AgBr was first predicted by Mott and Gurney.[1] The writer has measured the specific heat of AgBr (polycrystalline) from room temperature to its melting point (420°C). The heating velocity used was about 2°C per minute. A large increase in the specific heat was observed above 250°C, accompanying the production of lattice defects. The specific heat-temperature curve is shown in Fig. 1. The total energy required for the production of defects below 420°C was found to be 620 cal/M.

Generally, the number of defects in ionic crystals is thought to vary with the temperature according to the formula

$$n=n_0\exp(-A/kT). \tag{1}$$

When all of the defects are dissociated,[2]

$$A=\tfrac{1}{2}W_0; \tag{2}$$

and when all defects are associated to defect pairs,

$$A=W_0, \tag{3}$$

where W_0 is the energy required for the production of a pair of defects.

The anomalous specific heat is then given by the formula

$$\Delta C\propto T^{-2}\exp(-A/kT). \tag{4}$$

From the experimental results and Eq. (4) the value of A is found to be[3] (Fig. 2a)

$$A=17{,}200\text{ cal/M}.$$

This is much larger than the value $A=10{,}500$ cal/M which was obtained by Lawson[4] from Strelkow's data[5] on the thermal expansion of AgBr crystals.

As was pointed out by Lawson,[4] the presence of Schottky defects must be considered in order to explain the expansion data. The presence of Frenkel defects cannot be denied, however. Frenkel defects will make only a small contribution to the thermal expansion, but will make a considerable contribution to the specific heat. It is possible that the presence of both types of defects will lead to different activation energies for the specific heat and the thermal expansion.

The writer has examined Strelkow's data carefully and has found that in the temperature range above 300°C the value of A was 15,400 cal/M, and below 300°C it was 8500 cal/M (Fig. 2b).

Lawson has estimated that 4 percent defect sites should be present at 690°K. Using the value $A=15{,}400$ cal/M, the total energy required to produce these defects is 1230 cal/M from Eq. (2), and 615 cal/M from Eq. (3). This energy is expected to be smaller than the value 620 cal/M obtained from the specific heat, if the presence of both defect types is considered.

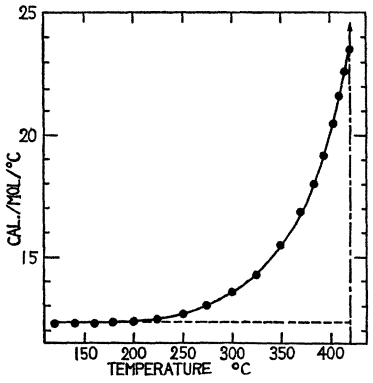

FIG. 1. Specific heat-temperature curve for AgBr.

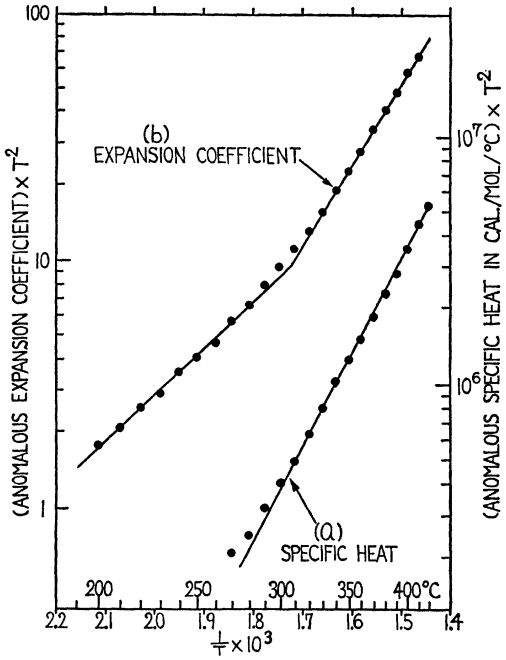

FIG. 2. (a) Anomalous specific curve in AgBr. (b) Anomalous expansion coefficient in AgBr (after Strelkow).

In consideration of the different experimental conditions, it seems certain that we must choose Eq. (3), rather than Eq. (2), for this temperature range of higher activation energy.

I am indebted to Professor R. Kubo for helpful suggestions and discussions.

[1] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1940), p. 48.
[2] Reference 1, pages 41 and 47.
[3] The activation energy for ionic conduction between 100°C and 300°C was 17,800 cal/M. The value given by Koch and Wagner is 18,200 cal/M (reference 1, p. 46).
[4] A. W. Lawson, Phys. Rev. **78**, 185 (1950).
[5] P. G. Strelkow, Physik. Z. Sowjetunion **12**, 77 (1937).

On the Aggregation of Trapping Centers in Semiconductors or Insulators

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IN semiconductors or insulators, the trapping energy of electrons changes with the aggregation of their trapping centers (impurity centers, F-centers, etc.). On this mechanism, the change of work function of BaO with activation and the production of A-, C-, D-, E-centers, etc., in KCl can be explained quantitatively.[1-3]

A hydrogen-like model was used as trapping center, and the Heitler-London method was used for the calculation of the aggregation process of more than two centers. In the case of the aggregation of more than three centers, only the energy of highest level in the case, in which each level is occupied in turn by an electron from the lowest level, was calculated. The highest energy is generally given by

$$E=W_0+\Sigma^{n-1}(C-J),$$

where W_0 is the first-order energy of electron, C and J are coulomb and exchange energies between the fixed center and any one of other centers, respectively.