

## Lattice Defects in Silver Bromide\*

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Measurements have been made of the lattice parameter of silver bromide at room temperature and in the range from about 350 to 420°C. The results are compared with the values obtained on the basis of two contrary assumptions: first, that the lattice expansion is identical with the external expansion measured by Strelkow; and second, that some of the external increase in volume is caused by formation of vacancies, the resultant parameter being that estimated by Lawson. Within experimental error, the measured curve agrees with the first assumption, which is equivalent to the assumption that no Schottky defects have formed. Since it is known from ionic conductivity measurements that there are about 2 percent of defects at temperatures near 420°C, it is concluded that these are Frenkel defects. However, the magnitude of the errors involved in the measurements is such that the existence of a small number (about 10 percent of the total) of Schottky defects cannot be entirely precluded.

### I. INTRODUCTION

SOME doubt exists concerning the nature of the defect structure of silver bromide. In the latent-image theory proposed by Gurney and Mott,<sup>1</sup> it was assumed that only Frenkel defects, consisting of interstitial silver ions and vacant silver ion sites, are present. However, a latent-image theory recently proposed by Mitchell<sup>2</sup> assumes that only Schottky defects, consisting of equal numbers of vacant silver ion and bromide ion sites, are important.

Much experimental and theoretical evidence has been presented to support the existence of one or the other type of defect structure. A few examples of this evidence will be given here.

Experiments on ionic conductivity of silver bromide at elevated temperatures reviewed by Tubandt<sup>3</sup> favor the existence of Frenkel defects. Also, Wagner and Beyer<sup>4</sup> report measurements of the x-ray lattice constant and the density of silver bromide near the melting point which indicate the existence of Frenkel defects.

On the other hand, an analysis by Lawson<sup>5</sup> of the data given by Strelkow<sup>6</sup> on the coefficient of expansion of silver bromide leads, with certain assumptions, to the conclusion that Schottky defects predominate near the melting point. Still other experiments on the orientations of silver produced in silver bromide by photolysis<sup>7</sup> indicate the existence of Frenkel defects in the pure crystals and the production of surface vacant anion sites during photolysis.

The present experiments were initiated to determine whether the two types of lattice defects could be distinguished at high temperatures by using the results

of measurements of the lattice constant of silver bromide to check the value of lattice constant reported by Wagner and Beyer,<sup>4</sup> and to test the assumption of Lawson<sup>5</sup> that the coefficient of expansion of silver bromide near the melting point is abnormal in the sense that the increase in volume of the crystals is caused partly by the production of lattice defects. The rather large number of defects<sup>8</sup> ( $\approx 2$  percent) present in silver bromide at temperatures near the melting point makes this a simple region to study by x-ray diffraction.

### II. EXPERIMENTAL PROCEDURES

Specimens of silver bromide were formed as thin surface layers on silver rods of about 0.8 mm diameter by reaction of the rods in bromine. The lattice parameters of silver and of silver bromide were determined at various temperatures. Because of the high absorption of copper  $K\alpha$  radiation in both silver and silver bromide, only a thin surface layer is effective in producing the diffraction patterns, the total effective thickness of silver bromide and silver being only about  $10\mu$ . Since this distance is so small, the reflections from the silver rod can be used to give an accurate calibration of the recording film and temperature determination of the silver bromide.

The temperature of the silver rod relative to 25°C was determined by comparing the lattice-constant change with the data on the expansion of silver given by Scheel,<sup>9</sup> assuming the number of vacant silver lattice sites at these temperatures to be negligible. That this assumption is valid can be seen by an examination of the defect structure of copper, which is similar to that of silver and whose melting point and activation energy for self-diffusion are near those of silver. The detailed calculations of Huntington<sup>10</sup> give an activation energy for vacancy formation in copper of 1.5 to 1.8 ev. Even if the activation energy for vacancy formation in silver were as low as 0.7 ev, the fraction of vacancies would be less than  $10^{-5}$  at 425°C.

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<sup>1</sup> R. W. Gurney and N. F. Mott, Proc. Roy. Soc. (London) **A164**, 151 (1938).

<sup>2</sup> J. W. Mitchell, Phil. Mag. **40**, 249 (1949).

<sup>3</sup> C. Tubandt, *Wien-Harms Handbuch der Experimentalphysik* (Akademische Verlagsgesellschaft m. b. H., Leipzig, 1932), Bd. 1, 12, Teil I, p. 384.

<sup>4</sup> C. Wagner and J. Beyer, Z. physik. Chem. **B32**, 113 (1936).

<sup>5</sup> A. W. Lawson, Phys. Rev. **78**, 185 (1950).

<sup>6</sup> P. G. Strelkow, Physik. Z. Sowjetunion **12**, 73 (1937).

<sup>7</sup> C. R. Berry and R. L. Griffith, Acta Cryst. **3**, 219 (1950).

<sup>8</sup> F. Seitz, Phys. Rev. **56**, 1063 (1939).

<sup>9</sup> K. Scheel, Z. Physik **5**, 167 (1921).

<sup>10</sup> H. B. Huntington, Phys. Rev. **61**, 325 (1942).

At room temperature, the lattice parameters of silver and of silver bromide were found, correction for film shrinkage being made by the method of Straumanis and Mellis.<sup>11</sup> Many other types of errors were minimized by obtaining the values of the parameter extrapolated to  $\theta=90^\circ$ , using the graphical scheme of Nelson and Riley.<sup>12</sup> The same scheme was used at high temperatures for determining the silver lattice parameter, but the back-reflection lines of the silver bromide disappeared because of strong atomic vibrations. For this reason, the forward-reflection silver bromide lines were used, and such corrections were applied to the measured lattice parameters as were shown to be necessary from measurements of neighboring silver reflections.

### III. DISCUSSION OF EXPERIMENTAL RESULTS

The lattice constants of the silver and of silver bromide, corrected for refraction and to a temperature of  $25^\circ\text{C}$ , were  $4.0860 \pm 0.0004$  and  $5.7745 \pm 0.0004\text{A}$ , respectively. The lattice constant of pure silver under similar conditions was given by Jette and Foote<sup>13</sup> at  $4.08611 \pm 0.00008\text{A}$ , and values of the lattice constant of carefully prepared precipitates of pure silver bromide were found to be  $5.7743 \pm 0.0004\text{A}$ . In view of this agreement, it was assumed that impurities or lack of stoichiometric composition would have no significant effects on the lattice parameters measured at high temperatures.

In Fig. 1 the experimentally determined values of the silver bromide lattice constant at high temperatures have been plotted as a function of temperature, and a smooth curve has been drawn. The temperature of the specimen was determined from the increase in the silver lattice parameter from  $4.0861$  at  $25^\circ\text{C}$ . An error of  $0.0001\text{A}$  in the lattice constant gives a temperature error of about  $1^\circ\text{C}$ . Since the parameter of silver at high temperatures may be in error by about  $0.004\text{A}$ , the temperature uncertainty is  $\pm 4^\circ\text{C}$ .

Errors in the lattice parameters of silver bromide are much larger because of the lack of back-reflection lines. In general, the higher the temperature the greater is the error because fewer and less smooth lines appear. The

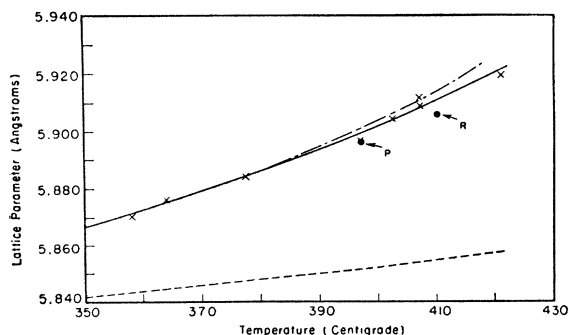


FIG. 1. Silver bromide lattice parameter. —, experimental; ----, crystals having no defects; - · - ·, assumed by Lawson.

<sup>11</sup> M. Straumanis and O. Mellis, *Z. Physik* **94**, 184 (1935).

<sup>12</sup> J. B. Nelson and D. P. Riley, *Proc. Phys. Soc. (London)* **57**, 160 (1945).

<sup>13</sup> E. R. Jette and F. Foote, *J. Chem. Phys.* **3**, 605 (1935).

effect is to give errors of about  $\pm 0.002\text{A}$  at  $360^\circ\text{C}$  and  $\pm 0.005\text{A}$  above  $400^\circ\text{C}$ .

The point, *P*, obtained from the x-ray measurements of Wagner and Beyer,<sup>4</sup> is in good agreement with present results. The uncertainty in the position of this point has not been given.

On the same diagram is plotted the curve obtained from Strelkow's<sup>6</sup> values of the coefficient of expansion of silver bromide, if it is assumed that the silver bromide lattice constant changes in the same way as does the exterior dimension. Otherwise stated, this would be the lattice constant of a specimen having no lattice defects; and in addition, to at least a first approximation, it would represent a crystal with Frenkel defects. From examinations of the random variations in Strelkow's data, it appears unlikely that the curve drawn here could be in error by more than  $\pm 0.002\text{A}$ . For comparison with Strelkow's data, the point, *R*, can be obtained from the observation of Wagner and Beyer<sup>4</sup> that the density of silver bromide is  $6.049\text{ g/cm}^3$  at  $410^\circ\text{C}$ , compared with  $6.476\text{ g/cm}^3$  at  $20^\circ\text{C}$ . If the value  $5.7743\text{A}$  is used for the lattice parameter at  $25^\circ\text{C}$ , a perfect crystal should have a parameter corresponding to the point, *R*. The average errors in the mean values of densities given by Wagner and Beyer would give an error of only  $\pm 0.002\text{A}$  in the lattice parameter. This discrepancy between the results of Strelkow and of Wagner and Beyer is apparently larger than would be expected on the basis of random errors, but its cause is not known.

The lowest curve is obtained from the coefficient of lattice expansion assumed by Lawson<sup>8</sup> to apply to a silver bromide crystal having no defects. According to Lawson's scheme, the production of Schottky defects should reduce the measured lattice constant still further.

Within the limit of possible experimental errors, the experimental curve is in agreement with the curve for a crystal having no defects or only Frenkel defects, and with the points, *P* and *R*; but it is completely at variance with the assumption made by Lawson. It is possible that all of the defects in silver bromide are Frenkel defects; but if the separation of the uppermost two curves were a real effect, it would correspond to a small concentration of Schottky defects. In this case, the fraction of vacant sites can be determined directly from the separation of the two curves, and is given by the relation:  $f = 3\Delta a/a$ . At  $415^\circ\text{C}$ ,  $\Delta a$  is about  $0.004\text{A}$ , and this corresponds to a fraction of vacancies,  $f = 0.2$  percent, compared with the number of defects that are known from the relation,<sup>8</sup>  $f = 29 \exp(-5050/T)$ , to be about 2 percent. It may be that Schottky defects are present to the extent of 10 percent of the total, but certainly Frenkel defects predominate.

The question of whether Schottky defects, or just vacant bromide ion sites, can be built into the crystal by artificial means, such as sulfur sensitization<sup>2</sup> or by photolysis,<sup>7</sup> is not answered by the present experiments.