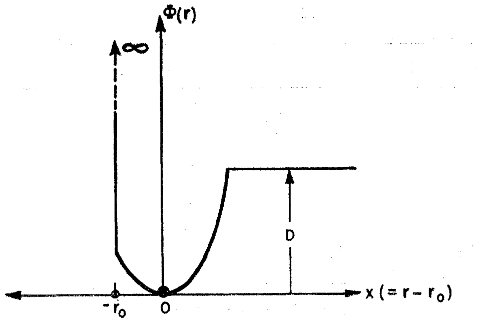

FIG. 4. Hypothetical form of interatomic potential.

ments but which predicts physically quite unrealistic behavior for the thermal expansion.

Specific Heat

Using $C_P=-T(\partial^2G/\partial T^2)_P$ with Eq. (3), we find

$$C_P=Nk\{1+\tfrac{3}{8}(5\lambda_3{}^2-4\lambda_4)kT/D+\cdots\},$$

and thus, using $C_P-C_L=T(\partial L/\partial T)_P(\partial P/\partial T)_L$,

$$C_{L;P\simeq 0}=Nk\{1+\tfrac{3}{4}(\lambda_3{}^2-2\lambda_4)kT/D+\cdots\}.$$

Introducing now the Lennard-Jones potential [see Eq. (4)], we obtain

$$C_{P;P\simeq 0}=Nk\{1+(1/12mn)(2m^2+2n^2+7mn+12m+12n+27)kT/D+\cdots\},$$

$$C_{L;P\simeq 0}=Nk\{1-(1/12mn)[(n-m)^2+nm+6m+6n+15]kT/D-\cdots\}.$$

Thus, for *all* $m,n>0$, $C_{P;P\simeq 0}$ is predicted to increase with T, whereas $C_{L;P\simeq 0}$ is predicted to diminish with T as found also in (I) for the Morse potential.

The general condition that the term in C_L linear with temperature should be negative may be written (see also Damköhler[6])

$$[\Phi'''(A_0)]^2>\tfrac{3}{2}\Phi''(A_0)\Phi^{\mathrm{iv}}(A_0).$$

This inequality is satisfied by both the Morse and Lennard-Jones potentials (whatever the values of n and m). We may therefore conclude, as foreseen in (I), that it is extremely unlikely that any physically plausible potential would give rise to a C_L increasing with temperature, in agreement with Damköhler's conclusions.

We are most grateful to Dr. J. S. Dugdale for many helpful discussions in the preparation of this paper.

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[6] G. Damköhler, Ann. Physik. 24, 1 (1935).

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Physical Defects in Silver Halides*

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The concentrations of imperfections in silver halides grown from the melt were investigated by comparing the measured densities with the ideal densities computed from the lattice dimensions. The density defect of the most perfect specimen of silver bromide was $\Delta\rho/\rho=-0.8\times10^{-4}$. The greatest amount of imperfection was $\Delta\rho/\rho=-18\times10^{-4}$ in a specimen of silver bromide containing about 4 mole percent silver iodide. Considering the effects of various configurations of voids, it seems reasonable to attribute most of the density defect in the best crystals to immobile aggregates of vacancies and to dislocations associated with small-angle mosaic structure. The contributions of large-angle grain boundaries and Schottky defects are negligible.

INTRODUCTION

THE concentration of imperfections in a crystal is of importance in determining many of its properties. In the silver halides considered here, the number of imperfections is undoubtedly closely associated with photographic behavior and with such related properties as optical absorption and electron- and hole-trapping.[1]

A direct method of obtaining information on the soundness of a crystal is to compare the measured density with an ideal density computed from the weight and volume of material in the unit cell. Straumanis[2] has recently reconsidered this type of measurement, and has determined the best values of atomic constants to use in the computations, assuming calcite to be a perfectly sound crystal.

The present investigation is a study of the defects at room temperature in pure specimens, prepared from the melt, of silver bromide, silver chloride, and solid solutions of a few mole percent silver iodide in silver bromide. Measurements reported by Keith and Mitchell[3]

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* Communication No. 1690 from the Kodak Research Laboratories.

[1] F. Seitz, Revs. Modern Phys. 23, 328 (1951).

[2] M. E. Straumanis, Phys. Rev. 92, 1155 (1953).

[3] H. D. Keith and J. W. Mitchell, Phil. Mag. 7, 42, 1331 (1951).

were interpreted as indicating a possible lack of soundness in silver bromide but hardly a significant amount compared with the experimental uncertainties. It seems likely that the concentration of impurities and imperfections in precipitates and emulsion grains will be somewhat greater than in the specimens crystallized slowly from the melt.

EXPERIMENTAL

Measurements of density were obtained from pieces of clear crystal containing only a few large-angle grain boundaries, but no cracks or bubbles. The specimens were prepared in various ways. One of the silver chloride crystals was drawn from the melt in air, and the other was obtained from the Harshaw Chemical Company. The silver bromide specimens were produced in different atmospheres by filtering the molten material through a Pyrex capillary and solidifying it in quartz. One of the silver bromoiodide specimens was formed after dripping part of the molten mixture through a capillary, and the other specimen was prepared by mixing and melting the material in a Pyrex beaker.

A representative silver bromide specimen and the two silver chloride specimens were examined for metallic impurities by spectroscopic analysis. In the silver bromide, silicon was the major impurity, and amounted to about one part per million. Slightly smaller amounts of calcium, magnesium, and lead were found, and only a few parts in ten million of iron, aluminum, cadmium, copper, and zinc were detected. Studies of the effects of silver oxide on the surface tension of molten silver bromide indicate that a few parts per million of silver oxide are probably present in those specimens which were not melted in the presence of HBr.[4] The level of impurities in the silver chloride was somewhat higher than in silver bromide, there being a few parts per million of aluminum, calcium, iron, silicon, and zinc. The main difference between the silver chloride grown here and that obtained from the Harshaw Chemical Company was the presence of lead in the Harshaw specimen to the extent of about 20 parts per million.

All of the specimens examined under crossed polarizers were slightly birefringent except one silver bromide crystal, which was carefully annealed.

Measurements of lattice parameter of silver bromide and silver chloride were made on powdered specimens with a General Electric Geiger Counter Diffractometer XRD-3. Each determination of lattice parameter was corrected for a variety of possible errors by using the extrapolation procedure of Nelson and Riley.[5] A correction for the refraction of the x-rays was applied.[6] The values of lattice parameter were obtained from the same material whose density was measured, except in the case of silver bromide. The value for silver bromide is the average of a large number of determinations made with specimens of various origins. There appear to be no differences of significance for the computations which follow in the values for photographic grains, gelatin-free precipitates, and annealed precipitates. The value for silver bromide at 25.00°C is 5.77475±0.00005 A.[7] The value for silver chloride is 5.55023±0.00005 A.

TABLE I. Lattice parameter and ideal density at 25.00°C.

AgBr	5.77475±0.00005 A	6.4753 g/cm^3±0.0002
AgCl	5.55023±0.00005 A	5.5667 g/cm^3±0.0002
AgBr-I 4.6%	5.7908 ±0.0005 A	6.4965 g/cm^3±0.0020
AgBr-I 4.0%	5.7884 ±0.0005 A	6.4931 g/cm^3±0.0020

A Straumanis-type powder camera was used for determining the lattice parameters of the silver bromoiodide specimens, since only a small quantity of powder was available for measurement. The values were not nearly so accurate as those obtained from the pure bromide and chloride, partly because of strains in the lattice which gave somewhat broadened diffraction lines.

The values of lattice parameter and of ideal density for all the specimens are given in Table I. The computations of the values of density of the mixed silver bromoiodide crystals depend on the compositions of the specimens. The fraction of silver iodide present was estimated from the known amounts of silver bromide and silver iodide added to the melts, and was checked by comparing the lattice parameters with values determined by Griffith and Berntson[8] relating composition to lattice parameter for coprecipitates of silver bromoiodide. The specimen mixed and fused in the beaker contained 4.0 mole percent iodide based on known weights of material in the melt, and on the lattice parameter. The other specimen contained 4.6 mole percent iodide according to the lattice dimensions, although 5.5 percent iodide was in the melt. This discrepancy may be caused by the tendency of the iodide to decompose rapidly when maintained at too high a temperature. The value, 4.6 mole percent, was assumed to be correct since it was obtained from filings of that portion of the solid actually used in the density measurements.

Measurements of density were made with a pycnometer having a volume of about 11 cm^3. Distilled water at 25.00°C was the displacement liquid. Flotation methods of density measurement do not appear to be

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[4] G. W. Luckey (private communication from the Kodak Research Laboratories).

[5] J. B. Nelson and D. P. Riley, Proc. Phys. Soc. (London) **57**, 160 (1945).

[6] A. J. C. Wilson, Proc. Cambridge Phil. Soc. **36**, 485 (1940).

[7] Values of lattice parameter of silver bromide at 25.0°C given in the literature recently, when compared on the basis of the copper $K\alpha$ wavelength of 1.54050 A, are: 5.7743—C. R. Berry, Phys. Rev. **82**, 422 (1951); 5.7743—H. E. Swanson and R. K. Fuyat, National Bureau of Standards Report 2508, 1953 (unpublished); 5.7748—J. Teltow, Z. physik. Chem. **195**, 213 (1950); 5.7749—H. D. Keith and J. W. Mitchell, Phil. Mag. **42**, 1331 (1951).

[8] R. L. Griffith and C. M. Berntson, Kodak Research Laboratories, have recorded in an unpublished report that the change in lattice parameter per mole percent iodide is $\Delta a = 0.00346$ A.

TABLE II. Density measurements and departure from the ideal values.

Specimen		Density, g/cm^3	Density defect, $\Delta\rho/\rho$
AgBr	X-ray value	6.4753	
AgBr	N_2 atmosphere	6.4746±0.0004	$(-1.1\pm0.9)\times10^{-4}$
AgBr	N_2 atmosphere	6.4741±0.0005	$(-1.9\pm1.1)\times10^{-4}$
AgBr	N_2, cold worked	6.4719±0.0005	$(-5.3\pm1.1)\times10^{-4}$
AgBr	HBr and Br_2 atmosphere while above mp	6.4748±0.0002	$(-0.8\pm0.6)\times10^{-4}$
AgBr	HBr and Br_2 above mp, N_2 annealed at 393°C, 64 hr, cooled to room temp. 40 hr	6.4736±0.0002	$(-2.6\pm0.6)\times10^{-4}$
AgBr-I 4.6%	X-ray value	6.4965	
AgBr-I 4.6%	N_2 atmosphere	6.4880±0.0024	$(-13\pm7)\times10^{-4}$
AgBr-I 4.0%	X-ray value	6.4931	
AgBr-I 4.0%	N_2 atmosphere	6.4814±0.0007	$(-18\pm4)\times10^{-4}$
AgCl	X-ray value	5.5667	
AgCl	Drawn in air	5.5655±0.0005	$(-2.2\pm1.3)\times10^{-4}$
AgCl	Harshaw	5.5645±0.0002	$(-4.0\pm0.7)\times10^{-4}$

feasible for the silver halides because of the lack of appropriate liquids having high density.

The measurements of density and the extent of the defects, which may be characterized by the relative change in density, $\Delta\rho/\rho$, are recorded in Table II. Each of the density values is the average of about ten individual determinations. The errors recorded are the probable errors of the mean. The rather large error in density in one case was caused by the small amount of specimen available. The few cases where the probable error was only ±0.0002 g/cm^3 were the last measurements, where improved experimental procedures were used. For comparison, Keith and Mitchell[3] gave the density of their specimen of silver bromide as 6.4752 g/cm^3.

In every case there is a density defect which is beyond the limits of experimental error. The smallest defect is $\Delta\rho/\rho=-0.8\times10^{-4}$, for the silver bromide kept in an HBr and Br_2 atmosphere when it was above the melting point. It is surprising that a similar annealed specimen has a greater concentration of defects. Straumanis[9] found that the departure from perfection of sublimed NaCl exceeded the experimental errors, and the imperfection expressed as a density defect was $\Delta\rho/\rho=-4.1\times10^{-4}$.

Although cold-working increased the density defect, the addition of silver iodide had a considerably greater effect. Even so, the imperfection is much less than the value of about $\Delta\rho/\rho=-1.3\times10^{-2}$ produced by adding 10 percent KBr to KCl.[10] Back-reflection Laue photographs were obtained with a beam having a diameter of 125 microns and a divergence of about 0.21 degree. Reflected beams from unannealed silver bromide and silver chloride were observed to contain fine structures and breadths, indicating mosaic misalignments of about 0.5° within the area covered by the beam. The breadths of the spots from the annealed specimen were somewhat smaller and not significantly greater than the divergence of the x-ray beam.

DISCUSSION

The concentration of impurities present does not appear to be sufficient to have a direct effect on the measured density. Reasonable configurations which could conceivably account for the observed lack of soundness of the crystals are isolated vacancies, groups of vacancies in arrays such as large-angle grain boundaries or collapsed disks, single-edge dislocations, and arrays of edge dislocations associated with small-angle grain boundaries. In the observed specimens, there is undoubtedly a certain amount of each of these configurations. The effect of each of these defects on the decrease in density will now be estimated.

If the decrease in density were attributed solely to Schottky defects, their concentration in pure silver bromide would have to be $-\Delta\rho/\rho=0.8\times10^{-4}$. It may be shown that this is far too high to agree with estimates of the concentration of mobile Schottky defects in silver bromide at room temperature. Extrapolation to room temperature of the ionic conductivity results of Koch and Wagner[11] indicates a silver vacancy concentration of about 1.2×10^{-6}, and these vacancies are not Schottky defects, but predominantly Frenkel defects,[12] which should have no differential effect on the ideal and measured densities. Thus, essentially none of the density defect in silver bromide may be attributed to Schottky defects.

In considering the nature of the vacancies in silver bromide, the bubble models of metal structures described by Bragg[13–16] and his collaborators are very helpful, although their description of the silver bromide structure is only approximate.

The models indicate that large-angle grain boundaries have associated with them a void region varying from one atom diameter at the points of greatest mis-

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match to zero at the points of good fit. Since this void volume is associated equally with the grains on the two sides of the boundary, we may consider that each grain is surrounded by a void sheath which has an average thickness of not more than one-fourth atom diameter. Considering cube-shaped grains with N atoms per edge, the change in density associated with the grain structure is

$$\Delta\rho/\rho = -\Delta V/V = -6(\tfrac{1}{4}N^2)/N^3 = -3/2N.$$

With grain sizes of a few millimeters or more in the specimens observed, N is about 10^7. So we can say with assurance that the effects of large-angle grain boundaries on the measured density defects in fused silver halides is negligible.

There may be an appreciable void volume associated with small-angle grain boundaries, however. The existence of mosaic structure has been indicated by studies of the width and intensity of x-ray reflection lines.[17] Although some mosaic structure exists in calcite from which Straumanis calculated the constants used in this paper, most crystals appear to have a more imperfect structure than calcite in this respect. Since small-angle grain boundaries appear to be composed of arrays of regularly spaced edge dislocations,[16] it is desirable to consider now the void volume associated with single edge dislocations.

Expansion at an edge dislocation is associated with the increased separation of planes of atoms which bound the slip plane. At the position of maximum distortion, the centers of the atoms have a separation equal to their diameter, D (assuming hard spheres), whereas their separation in the close-packed crystal is $(\sqrt{3}/2)D$. The difference is $0.13D$. The area associated with this separation of the planes depends on the length of the dislocation. If the lack of registry exists over a length of n atoms, the area increase will be $0.065nD^2$. Lomer[15] discusses the length of dislocations for metals, and he concludes that the value for copper is about five atoms. The dislocation length, according to Lomer's definition (the number of spaces where corresponding atoms or bubbles have lost contact), appears to be only about half the value required to describe the distance for the atoms to come into good register again. Then the value $\Delta A = 0.65D^2$ will be used as the increase in area at a dislocation.

The effect on the external volume of a crystal caused by an increase in volume at a singularity which causes a radial distortion has been discussed by Seitz[18] and Eshelby.[19] They find that the over-all expansion of the crystal is somewhat greater (1.5 to 1.8 times) than the increase in volume at the singularity. For a two-dimensional expansion, as with an edge dislocation, the two values of volume increase should be roughly equal.

Although the pattern of dislocations in silver bromide may be one in which the Burgers vector is in a [110] direction and the (111) plane is the slip plane, it is simpler, for rough computations, to picture the array of dislocations as forming cubic mosaics. Consider, then, a 1-cm cube having a concentration, C, of dislocations in each face. The change in density is then $\Delta\rho/\rho = -3C\Delta A = -2.0CD^2$.

The concentration of dislocation lines may be related to the size and misalignment of the mosaic elements in the following way: For square mosaic blocks which contain N atoms per side and an angle α between blocks, the number of dislocations along each edge of the block will be $N\alpha$. Since the total number of dislocations associated with each block is $2N\alpha$, the concentration will be $C = 2N\alpha/(ND)^2 = 2\alpha/ND^2$. The change in density associated with this concentration is $\Delta\rho/\rho = -2.0CD^2 = -4.0\alpha/N$. If the misalignment of the blocks is taken as $\alpha = 1/200$ radian, then, for the most perfect silver bromide specimen, N is 250 and the size of the mosaics is 1000 A (using for D the distance of closest approach of bromide ions). The mosaic size is not in good agreement with more common estimates of about 10 000 A, but it is interesting to note the mosaic sphere diameter of 2300 A for natural rock salt which was deduced from light-scattering measurements.[20] Although the present estimate of mosaic size is doubtless too small, it indicates that mosaic structure may be one of the more important configurations contributing to the density defect in silver bromide.

The failure of any of the configurations of voids which have been considered to account properly for the density defect leads to the supposition that most of the defect must be associated with immobile groups of vacancies. The number and size of such groups cannot be determined independently from density measurements, but might very well be determined from light-scattering.

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