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# Structure and Optical Absorption of AgI Microcrystals

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Large corrections to the x-ray intensities of the standard powder diffraction pattern of hexagonal AgI are proposed. Based on these intensities, it appears that some precipitates which have been described in the literature as pure hexagonal have actually contained about 30% of the cubic phase. Hexagonal AgI was produced during precipitation only by slow crystallization and without an excess of either $Ag^+$ or $I^-$. Faster precipitations gave mixtures of the cubic and hexagonal phases, and crystals whose average diameter was as small at 150 Å. The Rayleigh scattering of these suspensions was sufficiently small that the absorption coefficients of the crystals could be readily measured. The usually strong exciton absorption peak at about 420 mμ was missing in the small crystals. When the crystals were made to grow, the exciton peak appeared slightly below 420 mμ for crystals which became more hexagonal as they increased in size, and somewhat above 420 mμ for crystals which became more cubic. The decrease in absorption for AgI in the exciton region was much more than for the absorption edge of AgBr for crystals of comparable small size. Additional mechanisms for the loss of absorption in AgI compared with AgBr are apparently indicated. It is suggested that the exciton radius in AgI is so large that the exciton cannot be formed close to the surface.

## CRYSTAL STRUCTURE

PRECIPITATES of AgI at room temperature usually consist of a mixture of structures, hexagonal and cubic, according to the early work of Wilsey.[1] Recent work reported by Burley[2,3] and by Majumdar and Roy[4] shows that the cubic phase is only metastable and converts to the hexagonal phase in a time of several hours when the temperature is kept above 100°C but below 147°C, where an additional phase change to a high-temperature structure occurs.

A triplet of x-ray diffraction lines, occurring with copper radiation at diffraction angles between $22<2\theta<26$ degrees, has been useful in estimating the relative amounts of cubic and hexagonal phase.[2,4] All three lines occur in the hexagonal structure, but only the central line is present with cubic material. In attempting to use the relative intensities of these lines given by the National Bureau of Standards[5] for the hexagonal structure of AgI, an inconsistency arose. For a particular preparation of AgI, no combination of hexagonal and cubic structure could give our observed relative intensities, unless negative quantities of the cubic material were used. This suggested that the NBS sample of AgI was not pure hexagonal but contained some of the cubic phase. In fact, using the single-crystal intensity data of Burley[6] for hexagonal AgI, in the manner shown below, it appears that the NBS powder sample contained very close to 30% of the cubic phase.

In Fig. 1 there is plotted the ratio of intensity of the center line of the diffraction triplet to the sum of intensities of the two outside lines as a function of the fraction of cubic phase which is present. The theoretical (solid) curve which is plotted assumes the ideal (ZnS types) wurtzite and zinc blende structures of AgI where the $Ag^+$ ion layers are exactly $\frac{1}{4}$ of the way between neighboring iodide layers. This is the structure which Burley[6] found for hexagonal single crystals. Values of the crystal-structure factor which were used to compute the curve in Fig. 1 are the experimental values observed for single crystals of hexagonal AgI by Burley. We have assumed that the crystal-structure factors of (002) hexagonal and (111) cubic reflections are identical. The computed curve will be used in the work which follows to determine the relative amounts of hexagonal and cubic AgI from measurements of x-ray intensities.

According to the conclusions of Kolkmeijer and van Hengel,[7] which have been quite widely accepted, more nearly cubic AgI is precipitated when $Ag^+$ ions are in excess and more nearly hexagonal AgI is precipitated from excess $I^-$. The situation is apparently not quite this simple, as indicated by points A, B, and C in Fig. 1. Experiments B and C, where AgI was precipitated in gelatin solution in excesses of $I^-$ or of $Ag^+$ of $0.1N$, indicate that the amounts of cubic AgI range only between 30 and 65%. The relative x-ray intensities of precipitate B, made with excess iodide, were indistinguishable from the values given in the NBS circular for hexagonal AgI.[5] In order to obtain a pure hexagonal precipitate, it was necessary to have no excess of $Ag^+$ or $I^-$ during the precipitation and to add the $AgNO_3$ and KI solutions slowly and simultaneously, as for precipitates A. The range of compositions shown for precipitates A was caused by some inadvertent changes in precipitation conditions during repeated experiments.

Since the cubic phase of AgI is only metastable at room temperature, it was expected that its appearance would be encouraged under nonequilibrium conditions, such as when the precipitation was done quickly. In this connection, Burley[2] noticed that cubic material was dominant in a specimen quenched from the melt,

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[1] R. B. Wilsey, Phil. Mag. **46**, 487 (1923).
[2] G. Burley, Am. Mineralogist 48, 1266 (1963).
[3] G. Burley, J. Phys. Chem. 68, 1111 (1964).
[4] A. J. Majumdar and R. Roy, J. Phys. Chem. **63**, 1858 (1959).
[5] H. E. Swanson, N. T. Gilfrich, M. I. Cook, R. Stinchfield, and P. C. Parks, Natl. Bur. Std. (U. S.) Circ. No. **539**, 51 (1958).
[6] G. Burley, J. Chem. Phys. **38**, 2807 (1963).
[7] N. H. Kolkmeijer and J. W. A. van Hengel, Z. Krist. **88**, 317 (1934).

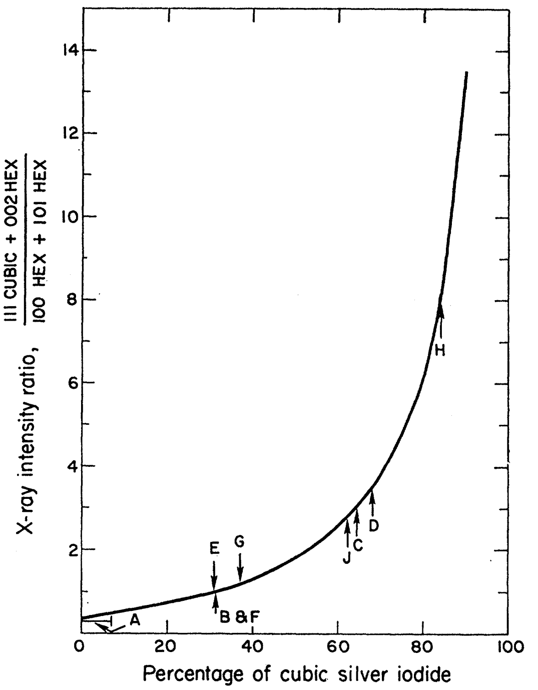

FIG. 1. Dependence of x-ray intensities on amounts of hexagonal and cubic AgI. Theoretical curve determined as discussed in the text. (A) Precipitations in gelatin, slowly, no excess of Ag$^+$ or I$^-$. (B) Precipitation in gelatin, slowly, excess of I$^-$. (C) Precipitation in gelatin, slowly, excess of Ag$^+$. (D) Precipitation in gelatin, fast, no excess of Ag$^+$ or I$^-$. (E) National Bureau of Standards, assumed to be pure hexagonal. (F) Large crystals (~0.1 mm) grown from HI very slowly (1 month). (G) Scrapings from thick evaporated film ($1.8\times10^{-4}$ cm). (H) Scrapings from thin evaporated film (650 Å). (J) Precipitation without gelatin, slowly, no excess of Ag$^+$ or I$^-$.

whereas hexagonal material was dominant with slow cooling. Precipitates made by rapid balanced addition of AgNO$_3$ and KI solutions in gelatin (point D) gave approximately 68% cubic material of extremely fine grain size (<200 Å in diam). The large breadth and overlap of the diffraction lines made the exact intensities uncertain in this case. Precipitates made by slow balanced addition of AgNO$_3$ and KI but without gelatin present (point J) to prevent coagulation and Ostwald ripening gave 62% cubic material. The only conditions of precipitation which produced entirely hexagonal crystals were when gelatin was present and the solutions were added slowly without an excess of either Ag$^+$ or I$^-$.

## OPTICAL ABSORPTION

The absorption of AgI microcrystals was of interest because recent measurements for microcrystals of AgBr gave values which were definitely different from bulk material.[8] Suspensions of AgI crystals of about 100–300 Å in diam were sufficiently weak in Rayleigh scattering that the absorption coefficients could be determined readily in the manner indicated previously.[8] The measurements were made with a Cary 14 Spectrophotometer at room temperature.

At somewhat shorter wavelengths than 430 mμ, the bulk absorption of AgI rises very rapidly to an exciton peak. Curve A in Fig. 2 gives the absorption coefficient of AgI as measured by Schell.[9] His specimen was prepared by treating a silver deposit with iodine vapor. We were unable to detect any difference between this curve and a measurement we made with an evaporated film of 650 Å thickness, which contained 84% cubic material, as indicated by point H in Fig. 1. (Although the amount of cubic phase could have been altered somewhat by scraping the material from its support, a dominant cubic structure is also indicated by the position of the exciton peak, as discussed below.) Curve A in Fig. 2 is the bulk absorption of AgI which is given in Ref. 10.

For comparison with the bulk absorption, curve B in Fig. 2 was obtained for a suspension of AgI, in which the average crystal diam was about 150 Å and the average thickness of AgI in the light beam was $4.66\times10^{-5}$ cm. It is interesting that there is no indication of the exciton peak in crystals of this size.

When the crystals of AgI in suspension were allowed to stand for several hours, the average size was in-

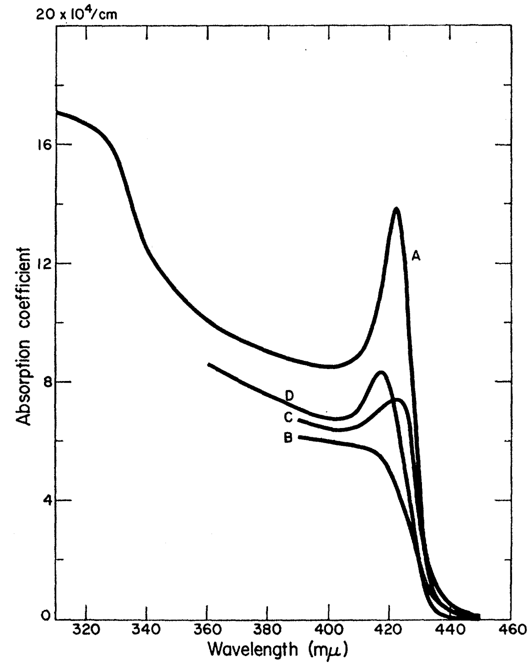

FIG. 2. Absorption coefficients of AgI in the wavelength region of exciton absorption. (A) Bulk absorption. (B) Suspension of dominantly cubic crystals with an average diam of 150 Å. (C) Suspension of dominantly cubic crystals with an average diam of 318 Å. (D) Suspension of dominantly hexagonal crystals with an average diam of 299 Å.

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[8] C. R. Berry, Phys. Rev. **153**, 989 (1967).

[9] C. Schell, Ann. Physik **35**, 695 (1911).

[10] *International Critical Tables*, edited by E. W. Washburn (McGraw-Hill Book Company, Inc., New York, 1929), Vol. 5, p. 270.

creased by the Ostwald ripening process (in which the larger crystals grow and the smaller crystals disappear, driven by the decreasing surface energy). The absorption coefficients of two of these suspensions of larger crystals are shown in curves C and D in Fig. 2. Some exciton absorption is quite evident in C and D. The peak positions are somewhat different in the two cases because the Ostwald ripening was done under somewhat different conditions, which gave different amounts of hexagonal and cubic structure. The peak at 417.5 m$\mu$ resulted from growth at room temperature for 24 h after addition of KI to give a concentration of $5.6\times10^{-3}$ $M$. The average crystal diameter increased from 150 to 299 Å and the structure changed from about 80% cubic to 90% hexagonal. The peak at 422.5 m$\mu$ resulted from growth at 50°C for 4 h with no addition of excess $Ag^+$ or $I^-$. In this case the average crystal diameter increased from 150 to 318 Å and the structure changed from 70% cubic to 100% hexagonal. The peak at 422.5 m$\mu$ resulted from growth at 50°C for 4 h with no addition of excess $Ag^+$ or $I^-$. In this case the average crystal diameter increased from 150 Å to 318 Å and the structure changed from 70% cubic to 80% cubic. The peak position given for bulk AgI in curve A is at 422.7 m$\mu$. This indicates that the specimen which Shell[9] prepared by treating a silver deposit with iodine vapor was predominantly cubic. The relative positions of the hexagonal (D) and cubic (C) exciton peaks are consistent with the observations on evaporated films at 4°K reported by Cardona.[11] Neither of the peaks is nearly as high or has as much area as for bulk material. However, since the peaks gradually grew with increasing crystal size, it is expected that they would eventually approach the bulk value. Because the turbidity also increased with crystal size, the growth of the exciton peaks could not be followed to larger crystal sizes than those shown in Fig. 2.

To get a quantitative idea of how the size of the exciton peak depends on crystal size, we estimated the amount of exciton absorption by taking the area under the peak. The baseline was set in an arbitrary way by extrapolating to long wavelength the values of absorption coefficient below 405 m$\mu$. In this way we concluded that peaks C and D in Fig. 2 have areas which are about 32 and 39% as large, respectively, as the peak for bulk AgI.

## DISCUSSION

The changes in absorption coefficient compared with the bulk values which were reported earlier[8] for fine crystals of AgBr were substantially smaller for crystals of a given size than the decreases shown in Fig. 2 for AgI at about 420 m$\mu$, in the wavelength range of the exciton peak. The decrease in absorption for small crystals of AgI outside of the exciton range, as seen at a wavelength of 390 m$\mu$, is about the same as for AgBr. At the absorption edge of AgBr, where the electronic transitions are indirect and assisted by phonons, it was suggested that the decrease in absorption for small crystals could be the result of either changes in the phonon spectrum caused by the presence of the crystal boundaries or by changes in the crystal structure and of the conduction and valence bands near the crystal surfaces. According to the last point of view, the depth of the surface layer, differing from the bulk, which does not contribute to the absorption in the edge region of AgBr is 10–15 Å. If it is assumed that the presence of the surface acts in a similar way in AgI, by causing departure from bulk properties, then the depth of this region can be readily computed. Since this depth will be much larger in AgI than in AgBr, it is reasonable to anticipate that additional mechanisms will be involved in the loss in absorption in AgI.

The relation between the thickness $T$ of surface layer which is assumed to have different properties from those of the bulk, crystal radius $R$, and the fraction $f$ of bulk absorption is obviously: $4\pi(R-T)^3/3=4\pi R^3f/3$. Since there were distributions of crystal size in our specimens, the determinations of $T$ were actually made by using $\sum_i N_i(R_i-T)^3=f_iN_iR_i^3$. The distributions of crystal size were obtained from electron micrographs. A size distribution was not used directly but only after adjusting the scale to give the correct prediction for the measured amount of Rayleigh scattering. The measurement of Rayleigh scattering is considered a more reliable way of determining the average crystal size than by using the electron microscope,[12] especially for these specimens where there was some decomposition in the electron beam. (Carbon replication was not suitable for crystals of such small size.)

For curve C in Fig. 2, when the fraction of bulk exciton absorption is taken to be 39%, the thickness of the surface layer assumed to have different characteristics from the bulk is 61 Å. For curve D, the surface layer is 69 Å based on absorption amounting to 32% of the bulk value for cubic material (curve A). This is undoubtedly an overestimate because this specimen was predominantly hexagonal and Cardona's[11] measurements at 4°K show that the exciton absorption is smaller for bulk AgI in the hexagonal structure than in the cubic structure. For a curve situated between B and C, but not shown in Fig. 2, a surface layer of 63 Å was determined for a fraction of exciton absorption amounting to 23% of the bulk value. The amount of exciton absorption in curve B would need to be 10% of the bulk value to give the same value for the surface layer as just computed. The estimates of thickness of surface layer given thus far have been based on crystals of spherical shape. Electron micrographs show that most of the crystals are not spherical. A variety of outlines are apparent, but the exact shapes are uncertain. For

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[11] M. Cardona, Phys. Rev. **129**, 69 (1963).

[12] C. R. Berry and D. C. Skillman, J. Phys. Chem. **68**, 1138 (1964).

any shape which is not spherical, there must be a greater surface-to-volume ratio than for the sphere of the same volume. Any departure from spherical shape requires a thinner shell at the surface to arrive at the same amount of inactive volume in the crystal. For example, the depth of surface layer for a cube would be 81% of the value for a sphere of equal volume. For an octahedron, the value would be 84%, and for a tetrahedron, 67%. Since the shapes are not known, we chose an intermediate value of 80% for a correction. This gives 50 Å as the depth for which bulk properties may not be found.

An additional factor compared with AgBr which may play a part in the decreased exciton absorption of AgI is imperfection in the bulk crystal structure. Since the AgI is a mixture of both hexagonal and cubic material, there may well be stacking faults in the microcrystals. However, we do not think that this is a major factor for several reasons. First, indications are that specimens of bulk AgI which have been prepared by any method for optical measurements have a mixture of crystal structures. Also, the presence of the surface in the microcrystals should encourage disappearance of some types of imperfection. In addition, the slow growth of the microcrystals by Ostwald ripening should improve the crystal perfection. However, when 7 out of 8 crystals disappeared and slowly deposited on those remaining (when an increase in average diameter from 150 to 300 Å occurred), the departure from bulk behavior was still very large.

Another possibility for the decreased exciton absorption could be important if the exciton radius was large. This factor is simply that the presence of the surface does not allow sufficient space totally within the crystal for the coupled electron and hole to exist or to be formed near the surface. If this is the reason for the decreased exciton absorption in AgI, it implies that a distance of about 50 Å from the surface is involved. Of this amount, if 15 Å is attributed to processes suggested by the results with AgBr and by the decrease in absorption outside the exciton region at 390 mμ, then 35 Å is left. This implies an exciton radius of the order of 35 Å. This value is so large that it indicates an exciton radius not much different from the value of 28 Å given for CdS by Thomas and Hopfield.[13]

In an attempt to get a clearer insight into the behavior of AgI, some optical measurements were made with small crystals of CdS suspended in dilute gelatin solutions, whose exciton structure has been intensively studied.[13] The result of such an experiment with CdS crystals of about 50 Å diam is shown in Fig. 3, where there is a comparison of the fine-particle absorption with the bulk values reported by Dutton.[14] The absorption of the small crystals is quite different from the bulk, being much smaller in the exciton region but much larger in the longer-wavelength region. No such increase in absorption at long wavelengths was observed for AgBr. In AgI at long wavelengths it was difficult to tell the effect of crystal size on absorption because the absorption coefficient is so strongly structure sensitive, being several orders of magnitude greater for cubic than for hexagonal AgI. For a more informative comparison with AgI, it would be desirable to have CdS crystals of somewhat larger size than in Fig. 3. Unfortunately, we were not able to find conditions of slow Ostwald ripening for CdS which permitted controlled growth. We can only conclude from Fig. 3 that a drastic reduction in absorption coefficient in the exciton region is demonstrated by CdS when the crystals are not much larger than the exciton radius. The differences in shape of the exciton peaks for AgI and CdS for both bulk and small crystals make any quantitative comparisons quite uncertain. In summary, our results make it seem plausible but do not show conclusively that the exciton radius in AgI is quite large.

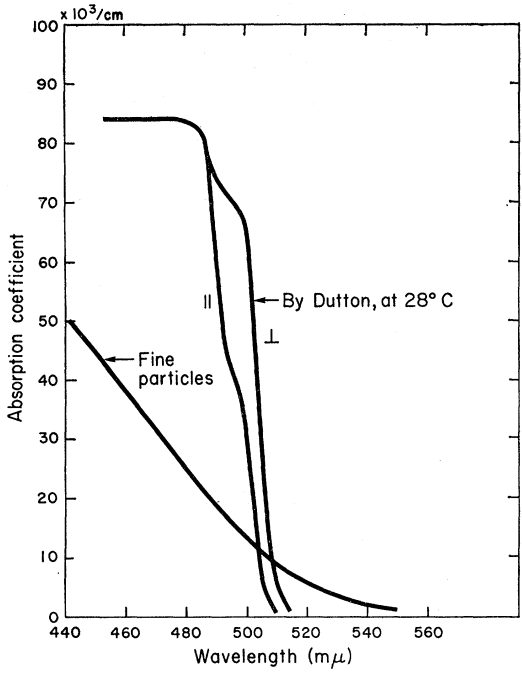

FIG. 3. Absorption coefficients of CdS in the wavelength region of exciton absorption. Bulk values measured by Dutton (Ref. 14). Crystals of about 50-Å diam in aqueous suspension.

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[13] D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).

[14] D. Dutton, Phys. Rev. **112**, 785 (1958).