Contribution from the Department of Physics, Department of Atmospheric Science, and Atmospheric Sciences Research Center, State University of New York at Albany, Albany, New York 12222

Investigation of the Pseudobinary Solid Solutions of AgI–CuI by Means of X-Ray Diffraction

HENRY CHESSIN,* RICHARD E. PASSARELLI, Jr., and BERNARD VONNEGUT

Received April 4, 1975 AIC50248R

AgI and CuI form a continuous solution throughout the entire composition range and a phase transition occurs in the crystal structures at elevated temperatures. Lattice spacings of the solid solutions have been determined by means of X-ray diffraction. The samples were prepared by vacuum fusion and by coprecipitation of the powders from solution. The shortest iodine–iodine distances bracket the shortest oxygen–oxygen distance in ice. The effectiveness of the solid solutions as nucleation catalysts increases with decreasing mismatch between the basal plane of ice and the (111) plane of the cubic solid solutions.

Recently it was shown by Chessin and Vonnegut[1] that the addition of silver bromide to silver iodide causes a significant decrease in the lattice spacings of the host silver iodide and conversely the addition of silver iodide to silver bromide causes an increase in the host silver bromide lattice spacings. This system forms two terminal solid solutions, but there is a large miscibility gap between these two solid solutions. Vonnegut and Chessin[2] showed that a significant improvement in nucleation ability occurred as the average distance of the atoms in the 111 plane of the AgI–AgBr solid solutions approaches that in the basal plane of crystalline ice. The observation was independent of the disregistry sign, δ, where δ is defined as

$$\frac{a - a_0}{a_0} \times 100$$

Here a and a_0 are the lattice parameters respectively of the catalyst and of ice in the aforementioned planes. It appeared that the degree of supercooling was symmetric about the position $\delta = 0$, but unfortunately this could not be observed rigorously because of the limitations of the solubilities of the two terminal solid solutions in the AgI–AgBr system. These findings support the theory suggested by Turnbull and Vonnegut,[3] who demonstrated that in the case of coherent nucleation catalysis, the structure of crystals, and the substances that catalyze their formation closely resemble each other in atomic arrangement and lattice spacings on low-index planes. Their crystallographic theory of crystal nucleation catalysis predicts that the order of catalytic potency should be identical with the order of the reciprocal of the disregistry between catalyst and forming crystal. It was, therefore, considered worthwhile to choose a system which exhibited complete solid solubility to see if the supercooling did indeed reach a minimum at zero disregistry. Such a system is AgI–CuI. The phase diagram is shown in Figure 1 and is taken from the work of Quercigh.[4]

Below the liquidus–solidus lines exists the cubic structure whose structure is not known, which is followed at the lower temperatures by a transformation to the hexagonal wurtzite structure over a relatively narrow temperature region. On further cooling to room temperature, a further phase transformation takes place from the wurtzite to the cubic zinc blende structure.

Specimens for this study were prepared in two different ways. In the first, the powders were mixed intimately and sealed off in a quartz tube under vacuum (10^{-2} mm Hg). The specimens were heated to a temperature approximately 20° above the liquidus for 1 hr, furnace-cooled to 5° below the solidus, and quenched in ice water. The second preparation involved coprecipitation from aqueous solutions. Suitable proportions of high-purity AgI and CuI were dissolved in hydriodic acid and precipitation was allowed to take place by boiling off the solvent. The fused salts were ground to a powder in a mortar and pestle. All specimens were passed through a 325-mesh screen and sealed off in thin-walled 0.5-mm diameter quartz capillaries.

Table I. Lattice Parameters and Distance of Closest Approach of the Atoms[a]

Sample	Mol % CuI	a_0, Å	DCA,[a] Å	δ, %
AgI[6]	0	4.5834	4.5834	1.549
Ice[7]		4.5135	4.5135	0
3	15	6.4413	4.5546	0.9106
4	20	6.4180	4.5382	0.5471
5	25	6.3952	4.5220	0.1883
6	30	6.3783	4.5101	−0.0753
8	40	6.3170	4.4668	−1.035
10	50	6.2551	4.4230	−2.005
13	65	6.2101	4.3912	−2.709
15	75	6.2096	4.3909	−2.716
CuI	100	6.0603	4.2853	−5.056

[a] The distance of closest approach, DCA, in the hexagonal system is the distance between like atoms in the basal plane given directly by the lattice parameter a_0. The distance of closest approach in the cubic system is $(2^{1/2}/2)a_0$, where a_0 is the lattice parameter. Disregistry between the crystalline lattice of the nucleating agent and the basal phase of ice is given by $\delta = (2^{1/2}/2)[a_0 - a_0(\text{ice})]/a_0(\text{ice})$.

X-Ray diffraction diagrams were taken in a 114.59-mm diameter Debye–Scherrer camera for 24-hr exposure employing a cobalt-target X-ray tube and an iron-foil filter to minimize the appearance of the Kβ lines on the diagram. The wavelengths used were $\lambda_{K\alpha}$ 1.79021 Å, $\lambda_{K\alpha_1}$ 1.78892 Å, and $\lambda_{K\alpha_2}$ 1.79278 Å. In addition, data were collected on an X-ray diffractometer employing a copper-target X-ray tube and a nickel-foil filter to reduce the Kβ radiation. A $^1/_2$° divergence slit, a 0.4-mm receiving slit, and a Tl-activated scintillation counter with pulse height selection were employed. Scanning was carried out at $^1/_2$°/min in 2θ. All the solid solution powder lines could be indexed on the basis of a face-centered cubic system, the phase corresponding to the room-temperature phase shown in the phase diagram. The pure AgI could not be indexed satisfactorily on the cubic system, especially at the high 2θ values but was satisfactorily indexed on a simple hexagonal lattice. The 2θ values extended out to 169°. It is likely, therefore, that the transformation cubic–hexagonal–cubic was extremely rapid and was not suppressed during quenching. No lines other than those belonging to the solid solutions were observed on the diagrams. The results of the X-ray diffraction analysis are shown in Table I. Figure 2 shows a plot of the distance of closest approach of the atoms plotted against mole percent of CuI. All data were corrected for camera radius error, for absorption of X-rays by the specimen, and for specimen eccentricity with respect to the primary beam by plotting the lattice spacings against the Nelson–Riley[5] function. For any one composition, the data

---

* To whom correspondence should be addressed the Department of Physics, State University of New York at Albany.

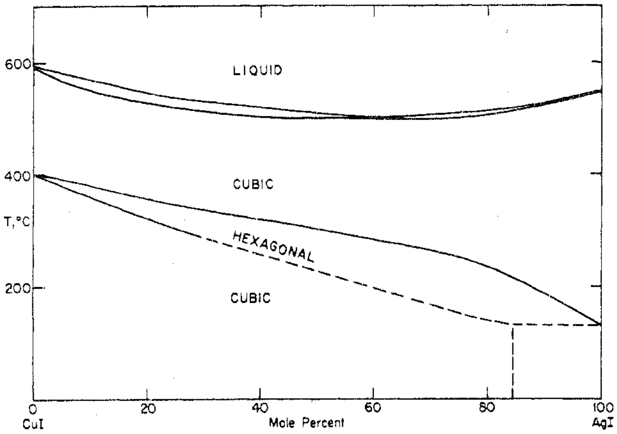

Figure 1. Phase diagram of the system of AgI–CuI according to Quercigh.[4]

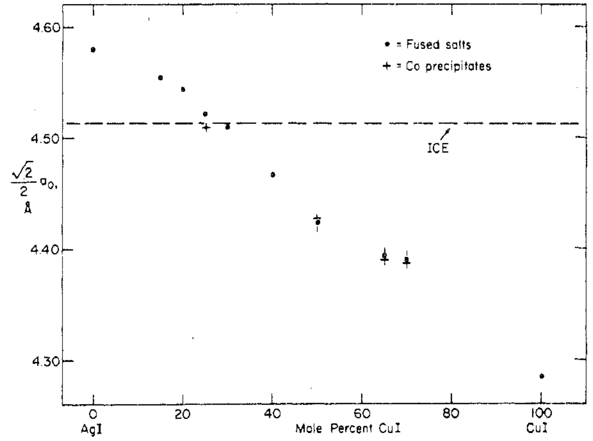

Figure 2. Lattice parameters, a_0, of the system AgI–CuI based on X-ray diffraction data. $(2^{1/2}/2)a_0$ is the distance of closest approach in the cubic system; in the hexagonal system it is given directly by a_0. The dotted line represents the distance of closest approach of atoms in the basal plane of ice.

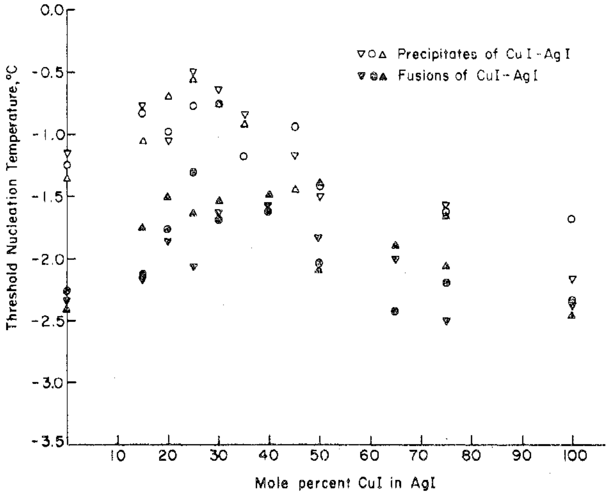

Figure 3. Threshold nucleation temperature as a function of composition.

collected four times agreed among themselves within 1 part in 8000, and it is estimated this is the degree of precision which can be attached to the data.

All of the films did not exhibit the usual sharp patterns observed when the specimens are of crystallite size, 0.1 μ, or larger and are free of internal microstress. The films and diffractometer traces showed distinct line broadening; increasing the patterns showed distinct sharpening of the lines. Further analysis is required to establish whether this effect is due to particle size or internal strain.

Figure 3 shows the observed threshold nucleation temperature, the highest temperature at which nucleation occurs, as a function of composition for the ten specimens listed in Table I for both the fused-salt and coprecipitated specimens. The three different symbols corresponding to precipitates or fusions correspond to the experiment repeated three times. The reader may therefore judge from Figure 3 the precision of the experiment. The temperatures for the fused salts were measured after the salts were kept in distilled water for about 1 month while the coprecipitates were tested immediately after preparation. Reduction of the cooling rates from 0.05° to 0.01°/min showed no differences in threshold nucleation temperatures. This latter phase of the work has been reported in more detail by Passarelli, Chessin, and Vonnegut.[8]

These studies lead to the following conclusions. The lattice parameters of the continuous solid solutions of AgI and CuI vary in a regular way from those of pure AgI to those of pure CuI. These findings are valid whether the solid solutions are prepared from the fused salts or the coprecipitated salts. The effectiveness of the solid solutions as nucleation catalysts increases with decreasing mismatch between the basal plane of ice and the (111) phase of the cubic solid solutions.

Acknowledgment. This work was sponsored in part by the Office of Naval Research under Contract No. N00014-71-C-0156 and in part by the National Science Foundation under Grant IO-34732.

Registry No. AgI, 7783-96-2; CuI, 7681-65-4.

References and Notes

(1) H. Chessin and B. Vonnegut, *J. Am. Chem. Soc.*, **93**, 4964 (1971).
(2) B. Vonnegut and H. Chessin, *Science*, **174**, 945 (1971).
(3) D. Turnbull and B. Vonnegut, *Ind. Eng. Chem.*, **44**, 1292 (1952).
(4) E. Quercigh, *Atti R. Accad. Naz. Lincei, Mem., Cl. Sci. Fis., Mat. Nat., Sez. I*, **23**, 831 (1914).
(5) J. B. Nelson and D. P. Riley, *Proc. Phys. Soc., London*, **57**, 160 (1945).
(6) J. D. Bernal and H. D. Megaw, *Proc. R. Soc. London, Ser. A*, **151**, 384 (1935).
(7) H. D. Megaw, *Strukturber.*, 3, 289 (1934).
(8) R. E. Passarelli, Jr., H. Chessin, and B. Vonnegut, submitted for publication in *Science*.