

lichten Untersuchungen bei Kristallitgrößen unterhalb von etwa 150 Å die Gitterkonstante von der Kristallitgröße abhängt.

4. Diskussion

Die am CsCl auf amorphen Unterlagen gewonnenen Ergebnisse stimmen mit den in der Einleitung zitierten Reflexionsuntersuchungen von Lüdemann auf kristallinen Unterlagen überein.

Dies gilt für die Abhängigkeit von der Aufdampfgeschwindigkeit und für die Umwandlung bei Erwärmung. Ein Unterschied gegenüber den Experimenten auf kristallinen Unterlagen besteht darin, dass auf amorphen Unterlagen nicht der NaCl-Typ allein erhalten werden konnte, weder in dünnen Schichten noch durch langsames Aufdampfen. Doch muss hierzu bemerkt werden, dass sehr dünne Schichten bei unseren Durchstrahlungsversuchen nicht erfasst werden können; zudem fehlt für einen Vergleich der Experimente in dieser Hinsicht eine genaue Kenntnis der verwendeten Aufdampfgeschwindigkeiten.

Unsere Untersuchungen zeigen, dass für das Auftreten des NaCl-Typs der Cäsium- und Thalliumhalogenide in dünnen Aufdampfschichten ein Einfluss periodischer Kräfte von der Unterlage her oder ein Gitter vom NaCl-Typ als Keim nicht notwendig ist. Die Beobachtungen zeigen ferner, dass der NaCl-Typ sich beim Erwärmen in den CsCl-Typ umwandelt und

dass durch schnelles Aufdampfen, bei dem infolge der raschen Bildung von Kristallen eine erhöhte Kondensationsenergie frei wird, die Bildung des CsCl-Typs bevorzugt ist. Dies deutet darauf hin, dass es von der zur Verfügung stehenden Energie abhängt, welcher der beiden Gittertypen gebildet wird. Es stellt also die NaCl-Modifikation eine instabile Phase dar, die bei Zuführung von Energie, entweder in Form einer von aussen zugeführten Wärme oder als Kondensationsenergie, in die stabile CsCl-Modifikation übergeht.

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The Thermal Expansion of Solid Bromine

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The lattice spacings of bromine have been determined over the temperature range -23.5°C . to -106.0°C . by the use of X-ray powder diagrams.

The expansion characteristics are found to be linear over this range and expressions are given for the coefficients of linear and volume expansion, as well as refined values for the lattice constants and density.

Introduction

Vonnegut & Warren (1936) have determined the lattice constants of a single crystal of bromine to three significant figures at a temperature which they estimated to be about -150°C . and have shown that bromine has the same structure as iodine. Although the coefficients of linear expansion for iodine are

known, they cannot be applied with great accuracy to the behaviour of bromine because of the slightly different axial ratios and molecular volumes of the two elements.

The present work seeks to refine the values for the lattice constants of bromine and to establish its principal coefficients of expansion.

Experimental

The bromine used in this work was purified through distillation with KBr, followed by storage in the presence of P_2O_5 for several weeks before use. Capillaries containing the liquid bromine were quenched in liquid nitrogen immediately before exposure in order to produce a fine-textured solid capable of yielding reasonable powder diffraction patterns from a rotated specimen.

The camera used was of special design, having a 9 cm. diameter film holder and made completely of brass. The specimen was supported and automatically centered in a 0.010" hole drilled in the center of the rotating spindle: this feature permitted the rapid insertion of the chilled specimen without recourse to the time-consuming task of manually centering the specimen before each exposure with the consequent danger of recrystallization or melting.

The temperature was measured by means of a previously standardized copper-constantan thermocouple placed near the specimen, and was controlled by means of various cooling baths which surrounded the entire camera. The temperatures of -23.5°C ., -53.0°C . and -78.5°C . were maintained by using cooling baths of freezing carbon tetrachloride, freezing calcium chloride solution, and solid carbon dioxide, respectively, while the temperature of -106°C . was obtained by surrounding the camera with sand into which small amounts of liquid nitrogen were poured as required.

Lattice parameter measurements

Cu $K\alpha$ radiation was used in conjunction with a slit collimator and the 9 cm. Bradley-Jay type camera mentioned previously. The specimen was rotated during exposure.

Each film yielded, on the average, about sixteen good diffraction lines, with Bragg angles up to 39° . Existing data on the lattice parameters of bromine by Vonnegut & Warren (1936) enabled these reflections to be indexed and distinguished from stray diffraction lines produced from the small amount of ice which condensed on the specimen and in the various parts of the collimator.

The lattice constants derived from these measure-

Table 1. *Lattice constants*

Temperature ($^\circ\text{C}$.)	a (\AA)	b (\AA)	c (\AA)
-23.5	4.548 ± 0.002	6.737 ± 0.003	8.761 ± 0.004
-53.0	4.533 ± 0.003	6.725 ± 0.005	8.746 ± 0.008
-78.5	4.517 ± 0.003	6.700 ± 0.004	8.748 ± 0.005
-106.0	4.498 ± 0.002	6.692 ± 0.005	8.737 ± 0.003

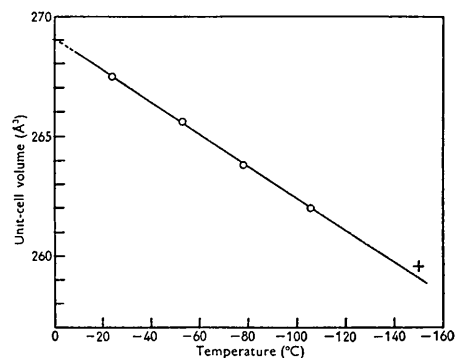


Fig. 1. Unit-cell volume of bromine as a function of temperature. ○ this work. + Vonnegut & Warren.

ments by the method of least-squares are listed in Table 1 while Fig. 1 shows the magnitude of unit-cell volume as a function of temperature. For purposes of comparison the unit-cell volume obtained by Vonnegut & Warren (1936) is included in the figure. Their value of 260.57\AA^3 is in excellent agreement with the present work when the expressed uncertainty of the temperature at which it was measured is considered.

Combination of the results by the method of least-squares yields the following expressions for the magnitudes of the lattice constants in \AA as a function of temperature:

$$a = 4.5636 + 6.074 \times 10^{-4}t \pm 0.0013$$

$$b = 5.7516 + 5.836 \times 10^{-4}t \pm 0.0018$$

$$c = 8.7649 + 2.590 \times 10^{-4}t \pm 0.0022$$

The coefficients of linear expansion are:

$$\alpha_a = 133.1 \times 10^{-6} \pm 0.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$$

$$\alpha_b = 86.44 \times 10^{-6} \pm 0.2 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$$

$$\alpha_c = 29.55 \times 10^{-6} \pm 0.1 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$$

and the volume coefficient of expansion is

$$\beta = 247.07 \times 10^{-6} \pm 0.10 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$$

and the density is

$$\rho = 3.924 - 1.062 \times 10^{-3}t \text{ g.cm.}^{-3}.$$

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