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Structure of the allotropic forms of strontium.

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Previous investigators have confirmed the face-centered cubic and the hexagonal close-packed modifications of calcium and have presented some evidence for the existence of one, or possibly two other forms. In a study of the phase diagram of the system calcium–barium by X-ray powder and thermal analysis, Sheldon & King (1949) have shown that a body-centered cubic form of calcium definitely exists at temperatures above 610° C. This finding prompted a study of strontium for which there had been little evidence for modifications other than the face-centered cubic form stable at room temperature. Cubicciotti & Thurmond (1949) observed a thermal pause in the cooling curve of pure strontium at 589° C. which they attributed to a transition. Rinck (1952) has recently concluded from electrical resistance, dilatometric and thermo-electric measurements that three allotropic forms of strontium exist with transitions at 235° and 540° C. No indication was given as to the structure of these new forms. The lattice constant of the face-centered form has been variously reported as 6·05 kX. by Ebert & Hartmann (1929), 6·03 kX. by Simon & Vohsen (1928, 1929), 6·075 kX. by King (1929) and 6·049 kX. by Klemm & Mika (1941).

The phase diagram of the system calcium–barium, as determined by Sheldon & King (1949), and of the system strontium–barium, under investigation by Hirst & Kanda (1952), show that all compositions between the two components in each case crystallize from their melts as a continuous series of solid solutions. Since barium crystallizes from its melt in a body-centered cubic lattice, it follows from the above that pure calcium and strontium must also have this structure just below their melting points.

The strontium used in this study was selected from the middle fraction of two to three pound batches sublimed in high vacuum. Its melting point was 770° C. Spectroanalysis showed approximately 0·3% barium and traces of Ca, Mg, Al, Sn, Mn and Fe. The strontium content by gravimetric analysis was 99·5%.

Diffraction studies at elevated temperatures were made with an X-ray powder camera similar in design to that described by Hume-Rothery & Reynolds (1938). The temperature of the specimen was measured continuously with a platinum–rhodium thermocouple welded to a cylindrical platinum band which was coaxial with the specimen tube. The thermocouple was calibrated, while mounted in the camera in its normal position just out of the X-ray beam, by observing the melting of standardized salts with the aid of a telescope.

Specimens of strontium were prepared by filing the metal and loading it into pyrex or Vycor capillaries in an atmosphere of purified argon, by a procedure similar to that of Raynor & Hume-Rothery (1934). The sample tubes were sealed off under approximately one-half an atmosphere of argon.

A number of individual specimens were investigated; some were carried through the series of transitions a number of times. After prolonged heating above 400° C. the inner wall of the capillary blackened, and lines of strontium oxide appeared on the diffraction pattern. This did not interfere with the reversibility of the transformations and had no detectable effect on the transition temperatures. It was assumed the blackening was due to a reaction between strontium vapor and glass and that this was confined to the walls of the capillary, since it did not seem to contaminate the bulk of the specimen.

Copper $K\alpha$ radiation ($\lambda\alpha_1 = 1{\cdot}53739$ kX.) was used throughout this study. Photographs were taken by the Straumanis method. The cell dimension of the low-temperature form was determined by extrapolation of data from photographs which showed good resolution in the back reflection region. The accuracy of the lattice constants at the higher temperatures was limited to $\pm 0{\cdot}01$ kX. units as the reflections at these temperatures were not sharp and none appeared beyond $\theta = 43°$.

Strontium was found to exist in three crystalline allotropic forms: face-centered cubic, hexagonal close-packed and body-centered cubic with transitions at $215 \pm 10°$ C. and $605 \pm 10°$ C. respectively. The cell dimensions found for these forms are:

α Sr F.-C.C. $a = 6{\cdot}0726 \pm 0{\cdot}0005$ kX. (25° C.),

β Sr H.C.P. $a = 4{\cdot}31 \pm 0{\cdot}01$, $c = 7{\cdot}05 \pm 0{\cdot}01$ kX. (248° C.),

γ Sr B.-C.C. $a = 4{\cdot}84 \pm 0{\cdot}01$ kX. (614° C.).

A few unaccountable lines were observed in the diffraction pattern in the immediate vicinity of the lower transition temperature. These may be due either to an intermediate modification, as suggested for calcium by Graf (1934), or to irregularities in the stacking sequence as the closest packed layers rearrange themselves in the course of the transition. A study of this anomaly is still in progress.

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