

THEORY OF CERIUM ISOMORPHISM. II. SINGULARITIES OF CERTAIN PHYSICAL PROPERTIES OF THE ISOMORPHOUS PHASES*

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Using the model of "pseudobinary solid solutions" developed in [6], the p - V - T relations have been studied for the isomorphous crystalline phases of cerium with a face-centered cubic lattice. A number of the anomalous properties of cerium have been explained: (1) the minimum coefficient of thermal expansion at atmospheric pressure; (2) the change in the coefficient of thermal expansion when the temperature and pressure vary from anomalously high to negative values; (3) increase in the compressibility of the phase, which is stable at low pressures, as the pressure rises.

Changes in the p - V - T relations of cerium have been observed by a number of investigators. Bridgman was first to show that, in contrast to all the other solids investigated, the compressibility of the high-pressure modification did not diminish at room temperature, but rises as a function of pressure. Bridgman's results were confirmed by Voronov, Vereshchagin and Goncharova by means of the ultrasonic method and Beecroft and Swenson by the static method [3], and they found that at room temperature the compressibility of α -Ce near the equilibrium line was greater than that of the high-pressure phase α' -Ce. According to Davis and Adams [4], at 470°C the opposite is observed: the compressibility of α -Ce is less than that of α' -Ce. According to the data of [5], the coefficient of thermal expansion of the β phase of α -Ce diminishes at low pressure in the range 300-500°K and rises at higher temperatures (minimum around 500°K). At the same time as the pressure increases, the coefficient of the β phase of α -Ce diminishes and, at pressures high enough, for instance, it becomes negative; the value of β rises for the α' phase as a function of pressure. At the same pressures it has an anomalously high positive value [4]. Even greater positive values of the coefficient of thermal expansion have been observed for cerium at a pressure of the order of 20 kbars [3]. The present article deals with analysis of the p - V - T singularities of the cerium relations, based on the model proposed in [5], according to which cerium is treated as a "pseudobinary" system, and the amorphous phases as solid solutions of variable concentration, based on components A and B (Ce^{4+} and Ce^{3+}).

Equations

The thermodynamic potential of the pseudobinary system will be given, in accordance with [6], as

$$G_C = (1 - C)(E_A - TS_A + pV_A) + C(E_B - TS_B + pV_B) + C(1 - C)U + RT[C \ln C + (1 - C) \ln (1 - C)] = E_C - TS_C + pV_C. \quad (1)$$

where C is the concentration of component B; U the energy of mixing. The extremal conditions for G_C gives the