7. BAND STRUCTURE OF CERIUM

Cerium metal has four allotropic modifications, two are face-centered cubic, one body-centered cubic and one hexagonal. The normal room temperature face-centered cubic form, γ-Ce, and the hexagonal form, β-Ce, have been suggested to have a valence of 3.05 [3] and presumably the high temperature body-centered cubic δ-Ce has also a similar valence. At low temperatures (~120°K and 1 atm) or at high pressure (~7.5 kb and 298°K) γ-Ce form transforms to the second face-centered cubic modification, α-Ce, with a large contraction in volume (17 to 12 per cent depending on pressure and temperature). This large volume change has been suggested by many to be due to the transfer of the 4f electron in cerium to the 5d band (see ref. 3 for a complete review of the pertinent literature). Gschneidner and Smoluchowski [3] have concluded from their examination of the physical properties of cerium and cerium-rich alloys that the valence of α-Ce is 3.67 at 1 atm and 116°K. Also in support of this valence for α-Ce are the calculations of Waber *et al.* [33] If these values are correct or nearly so, we may ask ourselves what is the band picture for α- and γ-Ce?

7.1 γ-CERIUM.

In order to explain the valence of 3.06 for γ-Ce one might suggest that there is a 4f one electron band which overlaps the 6s and 5d bands near the Fermi energy, such that about 0.06 of a hole exists in the 4f band and that the magnitude of the density of states is still governed by the 5d level. The order of magnitude of most of the observed physical properties of the cerium does not rule out this model. It is difficult to determine the sign and order of magnitude of the Hall coefficient on the basis of three overlapping bands since no mathematical solution has been proposed for this model. Infrared studies of γ-Ce at 298°K by Wilkins, *et al.* [34] revealed a large absorption at 15.5 microns, which they have not explained, and a number of minor peaks at shorter wave

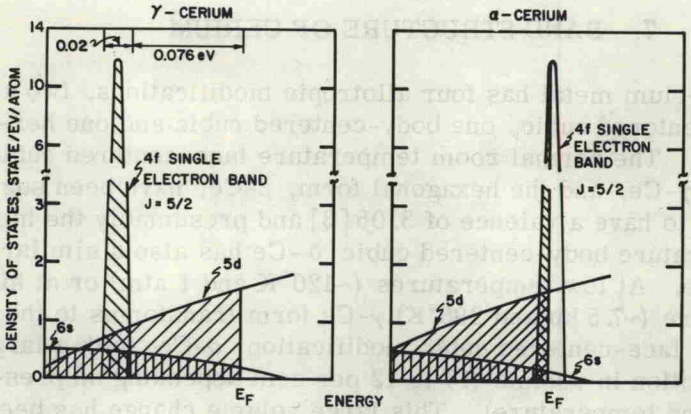

Fig. 6. Band structure of γ-Ce (a) and α-Ce (b).

lengths, which are probably due to intra-atomic transitions from the J = 5/2 (ground state) multiplet to the J = 7/2 multiplet. [35] The above model for cerium, however, is not capable of explaining this 15.5 μ absorption peak.

A model which is capable of explaining this and most of the observed physical properties is shown in Fig. 6a. The 15.5μ absorption would be due to the excitation of electrons from the narrow 4f single electron band to the 5d or 6s band at the Fermi level. The wavelength at which this transition occurs, suggests that the 4f level lies 0.076 eV below the Fermi energy and the width of the transition suggests that the one electron 4f band is very narrow, about 0.02 eV wide. The height of the 4f band is not known, but it is assumed to be higher than the density of states value obtained from the electronic specific heat constant of α-Ce (see Section 7.2). The Boltzmann distribution (exp $\Delta E/k\,T$) indicates that at room temperature 0.05 electrons are thermally excited to the 5d 6s band. This means that γ-Ce has an effective valence of 3.05, which is in very good agreement (better than one might expect) with the valence proposed by Gschneidner and Smoluchowski [3]. Since these authors based their valence on the magnetic properties and the atomic size of γ-Ce, these properties fit this model. Furthermore, since the