

earth metals--except, possibly, europium--a small, approximately temperature-independent paramagnetic susceptibility of magnitude  $1 \times 10^{-6} \text{ g}^{-1} \text{ cm}^2$  [*sic*, same as emu/gm] exists, and this originates from the conduction electrons."

From this it is seen that the magnetic susceptibility data of  $\gamma$ -Ce do not require the density of states of  $\gamma$ -Ce to be any larger than those of other rare earth metals.

From the above discussion it is concluded that the experimental resistivity and magnetic susceptibility data are consistent with the band structure proposed herein for  $\gamma$ -Ce as shown in Fig. 6a.

#### 7.2 $\alpha$ -CERIUM.

The non-integral value proposed for the valence of  $\alpha$ -Ce [3] suggests that about 60 per cent of the 4f electrons no longer occupy the one electron 4f band and are probably in the 5d band. A band structure which would take this into account is shown in Fig. 6b. In this model one would expect high density of states (much larger than 2.0 states/eV/atom) since the Fermi level would lie slightly below the middle of the 4f band. An examination and an analysis of the published low temperature specific heat data indicates that the density of states is indeed very large. (Fig. 7) At low temperatures ( $< 100^\circ\text{K}$ ) cerium consists of a mixture of  $\alpha$  and  $\beta$  phases. Because of this,  $\gamma$  values, which were obtained as the intercepts of the straight lines in Fig. 7, were assumed to be equal to the weighted sum of the  $\gamma$  value of each phase, i. e.:

$$\gamma = w_\alpha \gamma_\alpha + (1 - w_\alpha) \gamma_\beta \quad (16)$$

where  $w_\alpha$  is the fraction of  $\alpha$  in the sample. The electronic specific heat constant of  $\beta$ -Ce ( $\gamma_\beta$ ) was assumed to be 18 cal/g-at. deg<sup>2</sup>, the same as that of  $\gamma$ -Ce. The data of Parkinson *et al.* [41] yield a value of  $131 \times 10^{-4}$  cal/g-at. deg<sup>2</sup> for the electronic specific heat constant of  $\alpha$ -Ce; the data of Parkinson and Roberts [36] for their sample which had been cycled 50 times yield  $200 \times 10^{-4}$ ; and the data of

Lounasmaa [10] yield a mean value of  $138 \times 10^{-4}$  for his samples I and II. The amounts of  $\alpha$  and  $\beta$ -Ce present in the first two investigators' samples were not known and were estimated on the basis of the results of Gschneidner, *et al.* [37]. From X-ray measurements Lounasmaa, however, did give estimates of the amounts of  $\alpha$  and  $\beta$ -Ce present in his sample, and therefore, we feel that his value for the electronic constant of  $\alpha$ -Ce is the best available. By using Eqn. (3) a value of  $\gamma = 138 \times 10^{-4}$  yields a density of states of 12.2 states/eV/atom at the Fermi level of the 1/3 filled 4f one-electron band of  $\alpha$ -Ce. It is assumed since the band is only 1/3 filled that the top of this band is greater than 12.2.

Although there is a large variation in the  $\gamma$  values estimated in the above manner, the important thing is that they are all extremely large. This variation may be due, not only to the approximations involved in estimating the quantities of  $\alpha$  and  $\beta$ -Ce in the samples, but also to impurities which may change the electron concentration and thus the Fermi level. Any small change in the Fermi level would be expected to cause a large change in the density of states because of the narrowness of the 4f band.

With such a narrow band the high density of states of  $\alpha$ -Ce should be very sensitive to temperature and to impurities. Indeed by using the method of Mott [42], the degeneracy temperature of this band is calculated to be  $116^\circ\text{K}$ . Alloying studies would be very revealing if one could prevent the  $\beta$ -Ce from forming upon cooling. Indeed it would be desirable if one could obtain pure  $\alpha$ -Ce to measure the physical properties of it at low temperatures.

When  $\gamma$ -Ce transforms to  $\alpha$ -Ce it not only undergoes a large volume contraction, but also a large decrease in the electrical resistivity (from  $70 \mu \text{ ohm-cm}$  to  $30 \mu \text{ ohm-cm}$ ). This decrease in resistivity can be crudely accounted for by the increase in the number of conduction electrons (by about 2/3 of an electron per atom) and the decrease in the number of 4f electrons (by about 2/3 of an electron per atom), which give rise to the magnetic contribution to the resistivity. Interband scattering (s-f and d-f) would be expected to cause