

stant is related to the density of states,  $N(E)$ , for free electrons occupying a parabolic band by

$$N(E) = 3\gamma/2\pi^2 k^2 \quad (3)$$

where  $k$  is Boltzmann's constant. Stoner [8] has shown that Eqn. (3) is reasonably valid for any band form, except where the density of states varies rapidly with a small change in energy. The  $\gamma$  values for all of the elements have recently been summarized by Gschneidner [9] and are shown in Table I for the rare earth metals. Also included in Table I are some of the more recent values published by Lounasmaa [10, 11, 12] which differ considerably with the values listed by Gschneidner. [9] Examination of the  $\gamma$  values indicates a considerable variation as one proceeds along this series of elements, even if the values of  $\alpha$ -Ce, Eu and Yb are excluded because they are not trivalent metals. The corresponding density of states values are shown in Fig. 1, assuming Eqn. (3) is valid. Since the outer electrons of these trivalent metals are presumably the  $6s^2$  and  $5d^1$ , one would expect the density of states of these two bands to remain essentially constant for all the rare earth metals, as indicated by the horizontal dashed line in Fig. 1. If this is correct then the variation in the density of states must be due to the 4f electrons, which implies a broad 4f band which contains a number of peaks and valleys. (Fig. 1) The application of the rigid band model to the 4f transition metals would be expected to be valid in view of the success of this model for the d transition metals. [13, 14]. This means we could take the appropriate amounts of the two end-members, lanthanum and lutetium (ignoring crystal structure differences), and generate any of the other rare earth metals, e. g. a 13:1 atomic mixture of a La-Lu alloy (92.8 a/o La) would be equivalent to cerium, with one unpaired 4f electron, a magnetic susceptibility of about  $2.4 \times 10^{-3}$  emu/g-at. and a  $\gamma$  value of the order of 20 cal/g-at. deg<sup>2</sup>. The low temperature data of Anderson, et al. [15] for some La-Lu alloys indicate absence of any appreciable

magnetic moment and the presence of superconductivity (which excludes the presence of unpaired 4f electrons [16]) in alloys containing as much as 45 a/o Lu. These results and also other measurements made on different rare earth-rare earth alloys do not suggest a common band for the 4f electrons.

Perhaps the assumption that the  $\gamma$  values given in Table I are representative of the electronic contribution to the specific heat is not correct. In order to deal with this possibility we shall examine the various contributions to the specific heat. The lattice contribution to the specific heat at low temperatures has a  $T^3$  dependence, the nuclear  $T^{-2}$  dependence\* and the magnetic contribution can have either a  $T^3$  dependence for an antiferromagnetic material or a  $T^{3/2}$  dependence for a ferromagnetic substance. Rewriting Eqn. (1) as

$$C_p = C_v = \gamma T + BT^3 + CT^{-2} + DT^3 + ET^{3/2} \quad (4)$$

where  $D = 0$  for a ferromagnetic material,  $E = 0$  for an antiferromagnetic substance, and  $D = E = 0$  for a paramagnetic material. Of these contributions both the lattice and nuclear terms rest on sound theoretical grounds, but the magnetic contributions for these rare earth metals in view of their complex magnetic structures and possible Stark splitting of the ground states rest on very shaky ground. If the temperature dependence of one of four components of Eqn. (4) is incorrectly known, then the coefficients of the other terms will be incorrect. In view of the uncertainty of the magnetic contribution to the specific heats it would appear that the  $\gamma$  values obtained from the low temperature specific heat data of the magnetic rare earth metals are unreliable. Since trivalent lanthanum, lutetium, scandium and yttrium and divalent ytterbium are weakly paramagnetic, [2] Eqn. (4) reduces to

$$C_p = C_v = \gamma T + BT^3 \quad (5)$$

\* In some instances higher order terms, such as  $T^{-3}$ ,  $T^{-4}$ , etc., must also be included.