

DISCUSSION

The thermal expansion data presented in Fig. 1 and Table I reveal that CeRu₂ does not undergo any large volume changes that would be indicative of a large change in the electronic configuration of the cerium in CeRu₂ between room temperature and 900°C. The instantaneous coefficient of thermal expansion, however, shows (Fig. 2) that CeRu₂ expands at a faster rate than does LaRu₂ and PrRu₂ and that the value of α_t for CeRu₂ becomes larger than those of LaRu₂ and PrRu₂ above 375° and 225°C, respectively. This suggests that as the temperature is increased some of the valence electrons are transferred to the 4f band causing the cerium atom to increase in size. This increase in size would be in addition to that attributable to the normal expansion of the compound.

An estimate of the amount of electron transfer can be made in the following manner. The difference between the observed lattice parameter of CeRu₂ and the lattice parameter one would expect if it fell on the smooth curve drawn between the a values of LaRu₂ and PrRu₂ (*i.e.*, if cerium were trivalent in CeRu₂) is 0.1127 Å. We assume that this lattice constant difference corresponds to a valence change of 1 (*i.e.*, 4 to 3), and that any fractional change thereof gives us a fractional change of electrons. If we further assume that hypothetical CeRu₂ containing only trivalent cerium expands at a rate about equivalent to the mean of the expansion rates of LaRu₂ and PrRu₂, then we find that CeRu₂ would have a lattice parameter of 7.7186 Å at 900°C. Experimentally a value of 7.6143 Å is found. The difference between these lattice parameters is 0.1043 Å. From this value a valence of 3.93 is calculated for CeRu₂ at 900°C, assuming that cerium is tetravalent in CeRu₂ at room temperature. These numbers suggest that approximately 0.008 electron per 100°C are thermally excited from the valence band as the temperature increases.

Confirmation of the correctness of this analysis might be obtained by means of very precise high-temperature magnetic susceptibility data. By using eqn. (2) of GSCHNEIDNER AND SMOLUCHOWSKI² one would estimate a change in the effective moment of 0.03 Bohr magneton on heating CeRu₂ from room temperature to 900°C. This small change is very close to the experimental precision of most susceptibility apparatus. High-temperature specific heat data might be more informative since one would expect an excess of thermal energy from the promotion of electrons and an appreciable increase in the electronic contribution to the specific heat because of the filling of a very narrow one-electron 4f band, which has a very high density of states⁵.

REFERENCES

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