THERMAL EXPANSION OF LaRu₂, CeRu₂ AND PrRu₂ FROM 20° TO 900°C*

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SUMMARY

The lattice parameters of $LaRu_2$, $CeRu_2$ and $PrRu_2$ have been measured from approximately 20° to 800°, 900° and 650°C, respectively. The lattice parameters expand smoothly and continuously as the temperature is increased. $CeRu_2$, however, expands at a much greater rate than either $LaRu_2$ or $PrRu_2$. This greater rate is thought to be due to the transfer of 0.07 electron from the valence band to a one-electron $4f$ band by thermal excitation.

INTRODUCTION

Cerium metal is known to undergo an electronic transformation*** at either 1 atm and 116°K or 7,670 atm and 298°K[1,2]. This transition involves the transfer of about 0.6 electron per atom from the $4f$ band to the $6s5d$ valence band as the cerium is cooled or compressed[2]. For a number of intermetallic compounds cerium is known to be in the higher valent form at standard temperature and pressure. Thus, it was thought that heating one of these compounds might cause the cerium to undergo an electronic transformation from the tetravalent to the trivalent state. If a compound should undergo such a transformation then one would expect a large volume change to occur, which could be easily detected by thermal expansion measurements.

$CeRu_2$ was chosen as the compound to be studied because it has a cubic structure ($C15$, $MgCu_2$ type Laves phase) and because its lattice constant deviates farther from the smooth curve established for the corresponding trivalent RRu_2 Laves phase compounds (where $R = $ La, Pr, Nd etc.,) than do those of any of the other CeM_2 compounds (where $M = $ Mg, Al, Ni, Rh, Os, Ir and Pt) from the respective curves established for the RM_2 compounds. GSCHNEIDNER[3] shows that for CeM_2 compounds the difference between the theoretical lattice constants (for trivalent cerium only) and

the observed lattice constants (for higher than trivalent cerium) reaches a pronounced peak near $CeRu_2$. He explains this qualitatively by assuming that the $4f$ electron in a fraction of the atoms has been squeezed into the valence shell. This suggests that the cerium is probably more nearly tetravalent in $CeRu_2$ than in any other CeM_2 compound. $LaRu_2$ and $PrRu_2$ were examined as controls.

EXPERIMENTAL

Alloys were prepared by arc-melting together weighed amounts of the components. Filings for X-ray examination were taken from the arc-cast buttons and loaded into quartz capillary tubes, which were subsequently evacuated and sealed off. The filings were annealed at 450°C for 15 min to relieve stresses due to mechanical working before X-ray patterns were taken.

Two Unicam high-temperature X-ray powder cameras (190 mm diameter) were used to obtain X-ray diffraction patterns between 20 and approximately 550°C. A Central Research Laboratory (CRL) high-temperature X-ray powder camera (114.59 mm diameter) was used to obtain diffraction patterns at higher temperatures to 900°C. Specimen temperatures in the Unicam cameras were determined from calibration data relative to the furnace temperature, which was determined directly by means of thermocouples and potentiometric records. The calibration of the Unicam cameras was based on the lattice constants of pure silver as given by HUME-ROTHERY AND REYNOLDS[4] for a number of temperatures. The specimen temperatures in the CRL camera were determined from a power-setting *versus* temperature calibration curve, which was checked before and after each run. The calibrations were accomplished by placing a thermocouple in the sample position and noting the temperature corresponding to each power setting. No change in the calibration was observed throughout the experiment. Although the Unicam and CRL cameras were thus calibrated in different ways the lattice parameter data are in very good agreement where the temperature regions overlap (Fig. 1). Furnace temperatures were controlled within ± 2°C during each film exposure.

The lattice parameters were determined from Cu $K\alpha$ radiation back reflection doublets by using the φ tanφ extrapolation procedure. More than two-thirds of the lattice parameter measurements had standard deviations of ± 0.0005 Å or less; five had standard deviations greater than ± 0.0010 Å, the largest being ± 0.0015 Å. All lattice parameters were corrected for refraction.

CALCULATIONS

The temperature *versus* lattice constant data were fitted to an equation of the form

$$a = A + Bt + Ct^2 \tag{1}$$

by a least squares treatment. In eqn. (1) a is the lattice constant in Ångstrom units, t is the temperature in °C and A, B and C are constants. The average linear thermal expansion coefficient, $\bar{\alpha}$, is defined as

$$\bar{\alpha} = \Delta a/(a_0 \Delta t) \tag{2}$$

where a_0 is the lattice parameter at temperature t_0. Substituting eqn. (1) into (2) $\bar{\alpha}$

then becomes

$$\bar{\alpha} = (1/a_0) (B + C[t + t_0]) \tag{3}$$

where $t \neq t_0$. Equation (3) was used to calculate the average linear expansion coefficient for any desired temperature range within the range of the experimental measurements.

The instantaneous linear thermal expansion coefficient, α_t, is defined as

$$\alpha_t = (1/a_0) (\partial a/\partial t) \tag{4}$$

By taking the first derivative of eqn. (1) for a as a function of t, we have

$$\alpha_i = (1/a_0) (B + 2Ct) \tag{5}$$

Equation (5) was used to calculate the instantaneous linear thermal expansion coefficient for any desired temperature within the range of the experimental maesurements.

RESULTS

The X-ray patterns of LaRu$_2$, CeRu$_2$ and PrRu$_2$ showed two or three very weak front reflection lines in addition to the cubic Laves phase lines. These extra lines were indexed as ruthenium lines, in agreement with metallographic results which showed some undissolved ruthenium in the arc-cast buttons.

The lattice parameters as a function of temperature for each compound were measured to as high a temperature as possible and are shown in Fig. 1*. Reaction of the samples with the quartz capillaries limited the maximum temperatures that could be attained to 850°, 955° and 700°C for LaRu$_2$, CeRu$_2$ and PrRu$_2$, respectively.
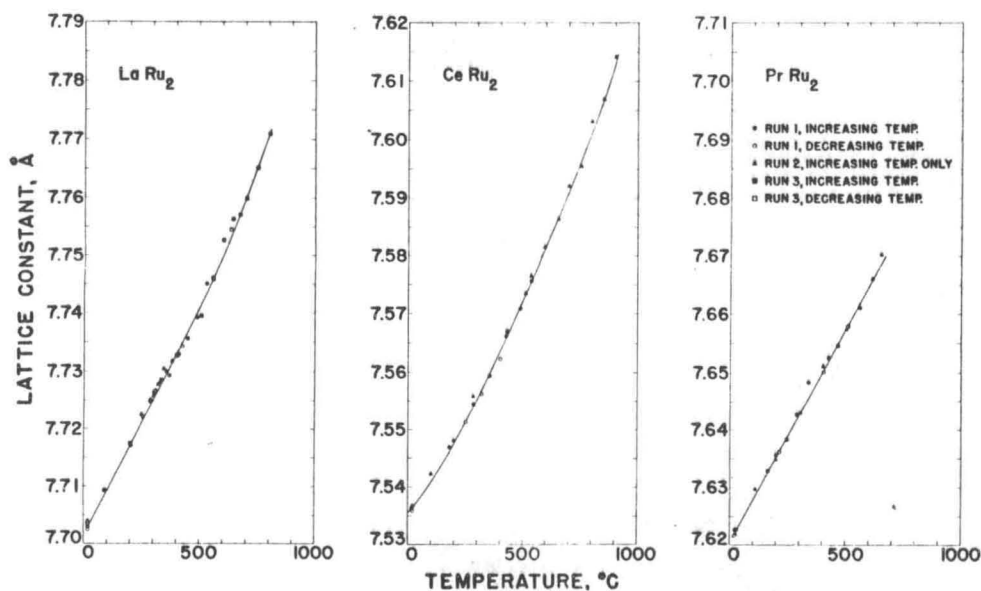

Fig. 1. Lattice parameters of LaRu$_2$, CeRu$_2$ and PrRu$_2$ as a function of temperature.

* The lattice parameter data are available upon request from the authors.

Lattice parameters obtained at these temperatures were excluded from Fig. 1 and from the least squares fits of the data.

The first run with LaRu$_2$ indicated that at about 300°C the lattice constant changed very little with temperature. In order to check this behavior a second run was made. The data from the second run, however, indicated no abnormal behavior at that temperature. This accounts for the high concentration of points shown near 300°C for LaRu$_2$ in Fig. 1.

The fits of the lattice constant *versus* temperature data are summarized in Table I. From these constants the instantaneous linear thermal coefficients were calculated by using eqn. (5). The resulting α_t values are shown in Fig. 2 as a function of temperature.

TABLE I

SUMMARY OF X-RAY THERMAL EXPANSION DATA

Compound	Temp. range (°C)	No. of points	$a = A + Bt + Ct^2$			Stand. dev. of fit $\sigma \times 10^4$ (Å)	$\bar{a} \times 10^{-6}/°C$ 20° to t_{max}
			A	$B \times 10^5$	$C \times 10^8$		
LaRu$_2$	16°–800°	38[a]	7.7025	7.021	1.75	±11.01	10.98
CeRu$_2$	19°–900°	26[b]	7.5354	5.700	3.31	7.72	11.59
PrRu$_2$	19°–650°	23[b]	7.6210	6.923	0.711	6.01	9.713

[a] Data obtained from Unicam cameras 1 and 2 and CRL camera.
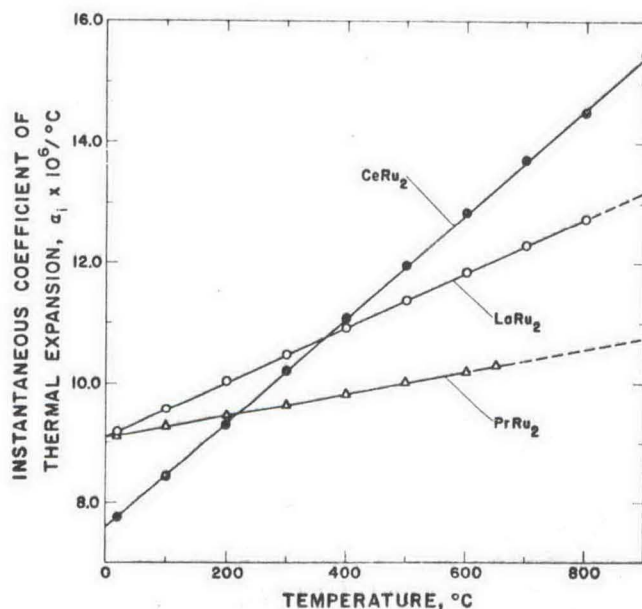[b] Data obtained from one of the Unicam cameras and the CRL camera.

Fig. 2. The instantaneous coefficient of thermal expansion of LaRu$_2$, CeRu$_2$ and PrRu$_2$ as a function of temperature.

DISCUSSION

The thermal expansion data presented in Fig. 1 and Table I reveal that $CeRu_2$ does not undergo any large volume changes that would be indicative of a large change in the electronic configuration of the cerium in $CeRu_2$ between room temperature and 900°C. The instantaneous coefficient of thermal expansion, however, shows (Fig. 2) that $CeRu_2$ expands at a faster rate than does $LaRu_2$ and $PrRu_2$ and that the value of α_t for $CeRu_2$ becomes larger than those of $LaRu_2$ and $PrRu_2$ 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 $CeRu_2$ and the lattice parameter one would expect if it fell on the smooth curve drawn between the a values of $LaRu_2$ and $PrRu_2$ (*i.e.*, if cerium were trivalent in $CeRu_2$) 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 $CeRu_2$ containing only trivalent cerium expands at a rate about equivalent to the mean of the expansion rates of $LaRu_2$ and $PrRu_2$, then we find that $CeRu_2$ 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 $CeRu_2$ at 900°C, assuming that cerium is tetravalent in $CeRu_2$ 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 SMOLUCHOWSKI[2] one would estimate a change in the effective moment of 0.03 Bohr magneton on heating $CeRu_2$ 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 states[5].

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