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LOW-TEMPERATURE LATTICE PARAMETERS OF THORIUM-CERIUM ALLOYS

Th – Ce

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and

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ROUGH DRAFT

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Abstract

The lattice parameters of a series of face-centered cubic alloys of cerium and thorium were measured at 93° and 298°K. Lattice parameters were also estimated for 171°K. Substantial deviations, y, from Vegard's Law were observed. Although y was negative at the two higher temperatures, it was positive and large at the lowest temperature. A variety of models, which have been proposed in the past, were considered, and the calculated values of y were compared with the observed values. The best agreement was achieved with values computed with Friedel's equation.

Introduction

The purpose of this investigation was to determine the effect of temperature on the lattice parameter and on deviations from Vegard's Law of cerium-thorium alloys. A large negative deviation from Vegard's Law was first observed by Weiner, Freeth and Raynor[1] in the room temperature lattice parameters of cerium-thorium alloys that form a continuous series of solid solutions. Their observation was confirmed by Evans and Raynor[2].

The allotropy of unalloyed cerium was reviewed recently by Gschneidner, Elliott and McDonald[3]. In two subsequent papers, these authors reported the influence of various alloying additions on the $\gamma \rightleftharpoons \alpha$ transformation, which occurs below room temperature. Although other rare earths tend to stabilize the double-hexagonal β phase, thorium, plutonium and scandium as solutes tend to stabilize the normal face-centered cubic γ phase. With addition of sufficient thorium as a solute, there is evidence that the formation of β is suppressed and it becomes possible to pass continuously with decreasing temperature from the room temperature γ phase to the face-centered cubic α phase*. Thus there is a closed β-loop which is similar in many ways to the γ-loop well known in ferrous alloys. A closed β field also occurs in the pressure-temperature "equilibrium" diagram of unalloyed cerium[3].

Because of interest in the effect of thorium additions and their influence on the α and β phases, lattice parameter measurements were

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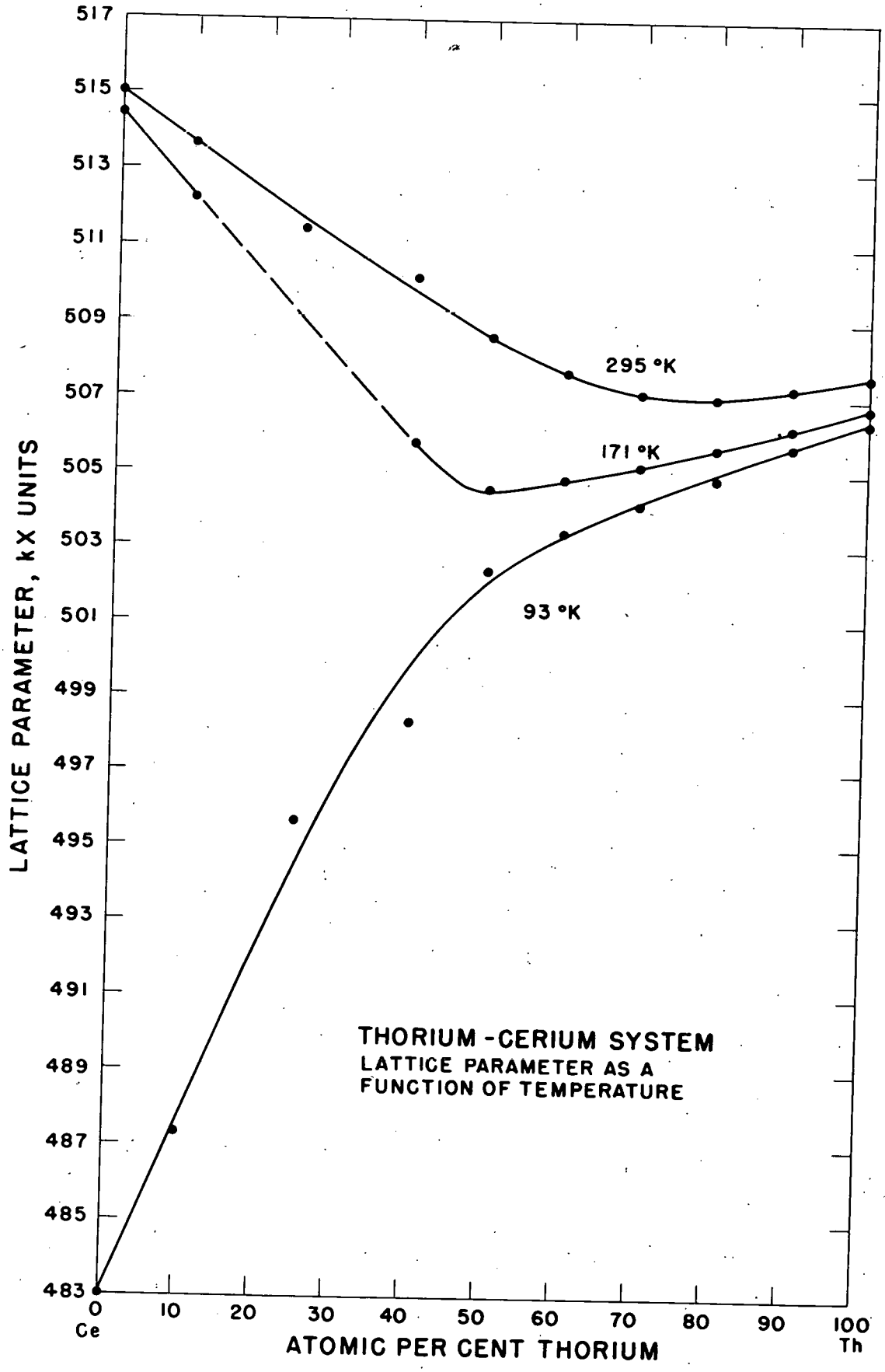
* In unalloyed cerium, the α phase is stable below 140°K and has a 16.7% smaller volume than γ, according to Gschneidner et al[3]. For convenience, we shall identify alloys having lattice parameters approaching 4.8 kx with increasing cerium content as α phase and those having lattice parameters approaching 5.1 kx as γ phase.

made at low temperatures on the face-centered cubic phase for a series of alloys ranging from 10 to 90 a/o thorium. The results obtained at three temperatures are shown in Figure 1.

Evans and Raynor analyzed the deviations from Vegard's Law in cerium-thorium alloys in terms of changes in the occupancy of the 4f band in cerium[2], which has been associated with the stability of the α phase[3,4,5]. They proposed that when the average interatomic distance in the matrix was smaller than the normal interatomic distance of cerium, strain energy could be reduced by the cerium atoms taking on a size more characteristic of the alpha or collapsed phase. The latter phase is stable under high pressure at room temperature. Their study of the influence of lanthanum additions to form ternary alloys[6] lent further support to their hypothesis; lanthanum is larger than thorium or cerium. Thus they could control the average interatomic distance in the matrix.

The deviations from Vegard's Law observed in the present study, which are negative at 300°K but positive at 93°K, were analyzed in terms of several models presented by Pines[7], Fournet[8], Friedel[9] and Sarkisov[10]. Recently Gschneidner and Vineyard[11] proposed a further model based on second order elasticity theory and compared the deviations predicted by several different models with experimentally observed deviations for a series of alloys of cerium with trivalent rare earths as well as with scandium and yttrium. Although most of the models predicted negative deviations, theirs led without exception to positive deviations. Investigating further, they

Fig. 1. The Lattice Parameters of the Continuous Series of Face-Centered Cubic Alloys of Cerium and Thorium, Measured at Three Temperatures, Versus Composition.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LATTICE PARAMETER, kX UNITS
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171 °K
93 °K
THORIUM - CERIUM SYSTEM
LATTICE PARAMETER AS A
FUNCTION OF TEMPERATURE
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ATOMIC PER CENT THORIUM

compared the experimental and predicted deviations for 15 binary systems involving two transition metals having the same valence. Since the predicted deviations were computed only for 2-a/o-additions of rare earths and for 10-a/o-additions of the transition metals, certain interesting features of the models were not observed.

It is a further objective of this paper to compare somewhat more fully the results obtained with the several models. Thorium-cerium alloys are quite suitable for this purpose because the atomic size and compressibility of α-cerium are so different from those of γ-cerium.

Experimental Details

High purity stocks of cerium supplied by Johnson-Matthey and iodide thorium supplied by the Atomic Energy Research Establishment were used in making the alloys. Pieces cut under carbon tetrachloride were weighed and placed (wet?) on the hearth of a large arc furnace. The furnace was quickly flushed with argon and evacuated to 10^{-3} torr (10^{-3} mm Hg). The pieces, which were wrapped together where feasible, were fused after an arc had been struck on a large piece of zirconium acting as a getter. The partially mixed pieces were alloyed and homogenized by inverting and remelting the buttons six times. The resulting buttons were wrapped in tantalum foil and homogenized at 1000°C for 1 week in a fused silica tube evacuated to 10^{-6} torr or better. The surface of each button was cleaned by filing, and the buttons were stored under carbon tetrachloride for later use.

Filings for X-ray diffraction examination were made under carbon tetrachloride and wrapped in tantalum foil to avoid contamination, following the procedure of Evans and Raynor[2]. The foil "capsules", wet with carbon tetrachloride, were placed in silica tubes which were then evacuated. When the pressure was reduced to 10^{-5} torr, heating was begun while the system was being continuously pumped. X-ray specimens were annealed for 4 hours at 900°C to relieve stresses.

A Phillips X-ray diffractometer was used with a geiger counter. The low-temperature attachment employed was a modification of the one reported by Butters and Myers[12]. The annealed filings were placed in the holder of the attachment and were carefully levelled. They were then moistened with a few drops of a dilute solution of Canadian balsam in xylene. When this cement dried, a razor blade was used to remove any excess filings above the reference level. The resulting level surface tended to be "rich" in balsam. Just before examination, a small quantity of annealed filings were dusted on the surface of the sample. This procedure increased the intensity of the diffracted beam above background.

The temperature of the specimen was measured with a copper-constantan thermocouple that had been silver-soldered into the surface of the brass block holding the specimen. The temperature was controlled by adjusting the flow of liquid nitrogen through the attachment. (Rex, was cooled gas used for the higher temperatures?)

Because of the design of the attachment, it was necessary to carefully align the specimen surface with the undiffracted beam for

each set of filings examined. One of the principal sources of error in obtaining precision lattice parameters occurred because the finished specimen surface was eccentric and lay above the axis of rotation of the X-ray diffractometer; measurements suggested that the displacement was a few ten-thousandths of an inch. The effect of this error on the lattice parameter could be minimized by using the Cos θ Cot θ extrapolation, as Parrish and Wilson[13] recommend. To increase the accuracy of angular measurements, the effects of shifts resulting from the characteristics of the rate-meter and the strip-chart were eliminated by scanning in both directions, and the mean peak position was employed in the calculation. The wavelengths of the Cu$K\alpha$ irradiation used in this calculation were 1.537 395 and 1.541 232 kγ.

Results

The lattice parameters at room temperature were also obtained by using standard film methods involving an 11 cm camera and the Nelson-Riley method of extrapolation. The lattice spacings obtained by the two methods are shown in Table I. Additional measurements were made after the powder specimens had been "quenched" in liquid nitrogen. The room temperature lattice parameters of samples containing from 50 to 100 a/o thorium were in excellent agreement with the room temperature values listed in Table I.

Lattice parameter values were obtained at a number of additional temperatures for alloys containing 10, 40 and 50 a/o thorium. These results are summarized in Table II.

The curve for 171°K in Fig. 1 was estimated from the parameter and coefficient of expansion data; the latter will be reported elsewhere.

Table I. Cerium-Thorium Alloy Lattice Parameters Obtained under Different Conditions

Nominal Composition a/o Cerium	Room Temperature Values		Values at 93°K
	Diffractometer	Camera	
0	5.0755	5.0755	5.0644
9.92	5.0735	5.0735	5.0580
20.00	5.0706	5.0707	5.0492
30.08	5.0720	5.0720	5.0418
39.95	5.0773	5.0773	5.0344
50.02	5.0867	5.0860	5.0242
60.03	5.1020	5.1020	4.9837
72.57	5.1143	5.1143	4.9567
91.09	5.1369	5.1365	4.8735
100.00	5.1507	5.1508	4.83

Table II. Variation of Lattice Parameters of Cerium-Thorium Solid Solutions with Temperature

10 a/o Th Alloy		40 a/o Th Alloy		50 a/o Th alloy	
T °K	Ao, kX	T °K	Ao, kX	T °K	Ao, kX
294.6	5.1362	293.1	5.1020	298	5.0867
250	5.1323	280.5	5.0967	281	5.0803
248	5.1331	226	5.0859	164.5	5.0428
236	5.1313	208	5.0788	97	5.0242
230	5.1315	191	5.0727		
227	5.1315	171	5.0585		
217	5.1298	....	.....		
151	5.1185	119	4.9846		
126	5.1078	109	4.9883		
....	.....	99	4.9858*		
93	4.8735	93	4.9838		

* Two identical values were obtained in duplicate experiments at this temperature.

The dotted lines signify the temperature ranges in which the $\gamma \rightarrow \alpha$ transformation occurred.

The low-angle diffractometer trace for the 60-a/o-cerium alloy showed that the α and γ phases were present at 93°K. Since the γ solid solution was the minor component, it may represent material that had failed to transform rather than the equilibrium situation.

As indicated in Table II, the 50-a/o-thorium alloy showed no variation of lattice spacing with temperature, which might be associated with the $\gamma \rightarrow \alpha$ transformation. This is not true for the 10- and 40-a/o-thorium alloys.

Inspection of the Ao-versus-T curves suggests that thorium additions raise the $\gamma \rightarrow \alpha$ transformation temperature and tend to eliminate the β phase. Weak β lines were observed in the low-angle diffractometer trace made at low temperature with the 10-a/o-thorium alloy but not with those containing 25 and 40 a/o thorium. The room temperature value for the latter composition only lies near the smooth curve drawn through the data. Although this may be due either to segregation of the thorium or an error in composition, it may also be intimately associated with a mixed $(\alpha + \gamma)$ region at 171°K.

It was observed that the room temperature lattice parameters of the thorium-rich alloys were unaffected by "quenching" the powder samples to liquid nitrogen temperature. However, a decided decrease in lattice parameter occurred in alloys containing 40 a/o thorium or less following this quench, and the decrease became greater with increasing cerium content. The cause of this phenomenon is not known. The resulting lattice parameters were too large to be

associated readily with the face-centered cubic γ-α intermediate phase reported by Gschneidner, Elliott and McDonald[3].

Comparison of Predicted Deviations from Vegard's Law

The models that have been proposed in recent years to account for observed deviations from Vegard's Law are primarily based on elastic theory. They lead to either positive or negative deviations depending upon the mechanical properties and the atomic size of the two alloy components. Two other models, which lead only to positive deviations, will be discussed first.

It is important to note that Raynor[14] pointed out, as others have, that Vegard[15] originally found that the molecular volumes of components in a binary system were additive. Subsequently, the more approximate formulation, namely that interatomic distances were additive, has come to be commonly accepted as Vegard's Law.

Zen's formula[16] for the lattice parameter, d, of an alloy

$$d = d_A \left\{ 1 - \left[1 - \left(\frac{d_B}{d_A} \right)^3 \right] C_B \right\}^{1/3} \qquad (1)$$

is based on the additivity of volumes and leads to positive deviations, y, from the linear or distance form of Vegard's Law. That is

$$y = d - (C_A d_A + C_B d_B) \qquad (2)$$

In these equations, C_A and d_A represent the atomic concentration and the lattice parameter of the solvent. Subscript B pertains to the solute.

Gschneidner and Vineyard[11] employed the pressure dependence of the shear modulus, μ, of the solvent to estimate the deviations. In their expression

$$d = (C_A d_A + C_B d_B) + \left(\frac{8\pi}{3}\right) nf^3 \left(\frac{d\mu}{dp} - \frac{\mu}{B}\right) C_A C_B \left[\frac{(d_A - d_B)^2}{(C_A d_A + C_B d_B)}\right] \quad (3)$$

B is the bulk modulus, n is the number of atoms per unit cell and f is the ratio between the atomic radius and the cell edge. For face-centered cubic lattice, $nf^3 = 2$. They point out that the term

$$\left(\frac{d\mu}{dp} - \frac{\mu}{B}\right)_A \simeq 2\mu \chi_A \gamma \quad (4)$$

where γ is the dimensionless Gruneisen parameter and χ_A is the compressibility of the solvent. With their expression, Gschneidner and Vineyard[11] predicted the sign and magnitude of the observed deviations substantially better for a group of 42 binary systems than could be done with the elastic models. Since effects due to differences in valence were not included in their theory, they limited their comparisons to alloy systems selected so as "..... to eliminate systems in which the end-members have different outer electronic structures, and in which deviations may be due at least in part to electronic effects."

Now it is interesting to compare the expressions proposed by Pines[7], Fournet[8] and Friedel[9]. Using an elastic sphere model, Pines suggested that

$$y = C_A C_B \left(d_B - d_A\right) \left[\frac{(4\mu_A/3)(\chi_A - \chi_B)}{1 + (4\mu_A/3)(C_B\chi_A + C_B\chi_A)}\right] \quad (5)$$

Starting with very general expressions for the energy of alloys, Fournet arrived at the formula

$$y = C_B(d_B - d_A)\left[\frac{\sqrt{d_B\chi_A} - \sqrt{d_A\chi_B}}{\sqrt{d_A\chi_B} + \sqrt{d_B\chi_A}}\right] \qquad (6)$$

Friedel's prediction is based on a strain analysis of the matrix after a foreign atom has been substituted for a solvent atom. He found that

$$y = C_B(d_B - d_A)\left(\frac{\chi_A - \chi_B}{\chi_B}\right) \Big/ \left[\frac{(1 + \sigma_A)\,\chi_A}{2(1 - 2\sigma_A)\,\chi_B} + 1\right] \qquad (7)$$

where σ is Poisson's ratio.

It is apparent that the sign of y in these equations is determined by the product, P, of Δd and $\Delta\chi$, which occur in the Pines and Friedel equations. When Δd and $\Delta\chi$ differ in sign, y becomes negative. Another criterion which is equivalent to P can be obtained from Fournet's expression. One further difference between these elastic models is that the Fournet and Friedel equations are linear in the solute concentrations C_B whereas the Pines equation is quadratic, i.e. it involves $C_B(1 - C_B)$. Apparently Sarkisov[10] has proposed the only theory for deviations that involves the valence of the solute and solvent and hence is electronic in nature.

His formula

$$y = K\left[\frac{C_A F_A^{1/3} + C_B F_B^{1/3}}{(C_A F_A + C_B F_B)^{1/3}}\right] - \left[C_A K_A \left(\frac{F_A}{f_A}\right)^{1/3} + C_B K_B \left(\frac{F_B}{f_B}\right)^{1/3}\right] \qquad (8)$$

is more difficult to use than the others, since the parameter F is given by

$$F = Z^{2/3} - z_f^{2/3} \qquad (4)$$

where Z is the atomic number and z_f is the number of f electrons in all elements with atomic number greater than 57, namely that of lanthanum. The quantity f, is the number of valence electrons and K depends on the crystal structure of the solid solution.

The physical constants of cerium and thorium used for estimating y by these several different methods are given in Table 3. The values

Table III. Physical Constants Involved in the Calculation of Deviations from Vegard's Law

Quantity and Units	Thorium	α Cerium	γ Cerium
Lattice Parameter, kx	5.0755	4.83	5.1508
Compressibility χ, $10^{-7}cm^2/kg$	18.18	5.76	49.2
Poisson's Ratio	0.25	0.18	0.248
Grüneisen's Constant	3.2	3.6	3.6
Shear Modulus, $10^{-6}kg/cm^2$	0.302	0.085	0.122

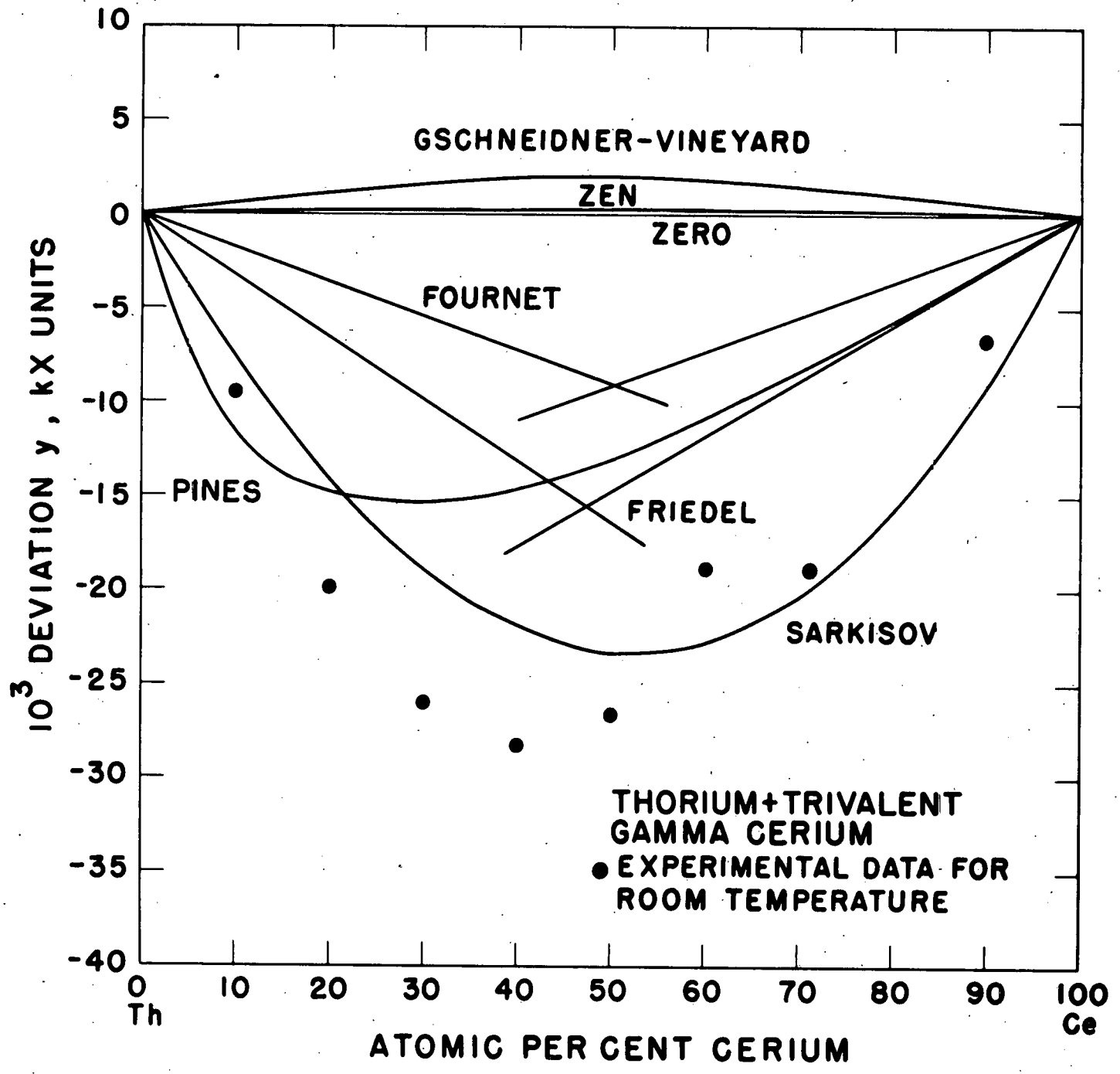
taken for Grüneisen's constant are large. The constant for thorium was estimated from compressibility data, and the constant adopted by Gschneidner and Vineyard for cerium was also used here for both phases. For α cerium, the Sarkisov parameters f_A and Z_f were taken to be 3.62 and 0.38, respectively. Because most of these physical properties have not been measured at liquid nitrogen temperature, it was necessary to use room temperature values in comparing calculated and experimental y values obtained at 93°K.

One such comparison is made in Figure 2. It will be seen here that the negative deviations observed at room temperature with γ solid solutions are definitely larger than those predicted by any of the models. In contrast, the large positive deviations seen in Figure 3 for the α solid solutions are in reasonable agreement with those obtained with Friedel's equation. In these two figures, the same vertical scale has been used to emphasize the difference in magnitude of the deviations. Only one of the two possible curves from Pines' theory was plotted to reduce clutter in these figures; the second curve would arise from substituting the shear modulus of either cerium phase for that of thorium. The Pines-Friedel criterion, $P \times 10^7$, was approximately 9.7 for α and -2.3 for γ solid solutions.

DISCUSSION

Evans and Raynor[2] discuss the fact that, although the atomic diameter of γ-cerium is larger than that of thorium, solution of cerium in thorium results in contraction that causes a minimum to occur in the lattice spacing/composition curve. They conclude that the cause for the contraction of the cerium atom can plausibly be associated with the promotion of a 4f electron into the 5d or bonding state. The necessary energy for such a transfer is gained from reducing the strain energy of the matrix. Essentially all of the published information (1) on the allotropic transformation of cerium at low temperature or at high pressure and (2) the magnetic

Fig. 2. Comparison of the Observed and Computed Negative Deviations from Vegard's Law for the γ Phase at Room Temperature.


10
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10^3 DEVIATION y, kX UNITS
GSCHNEIDNER-VINEYARD
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THORIUM+TRIVALENT GAMMA CERIUM
● EXPERIMENTAL DATA FOR ROOM TEMPERATURE
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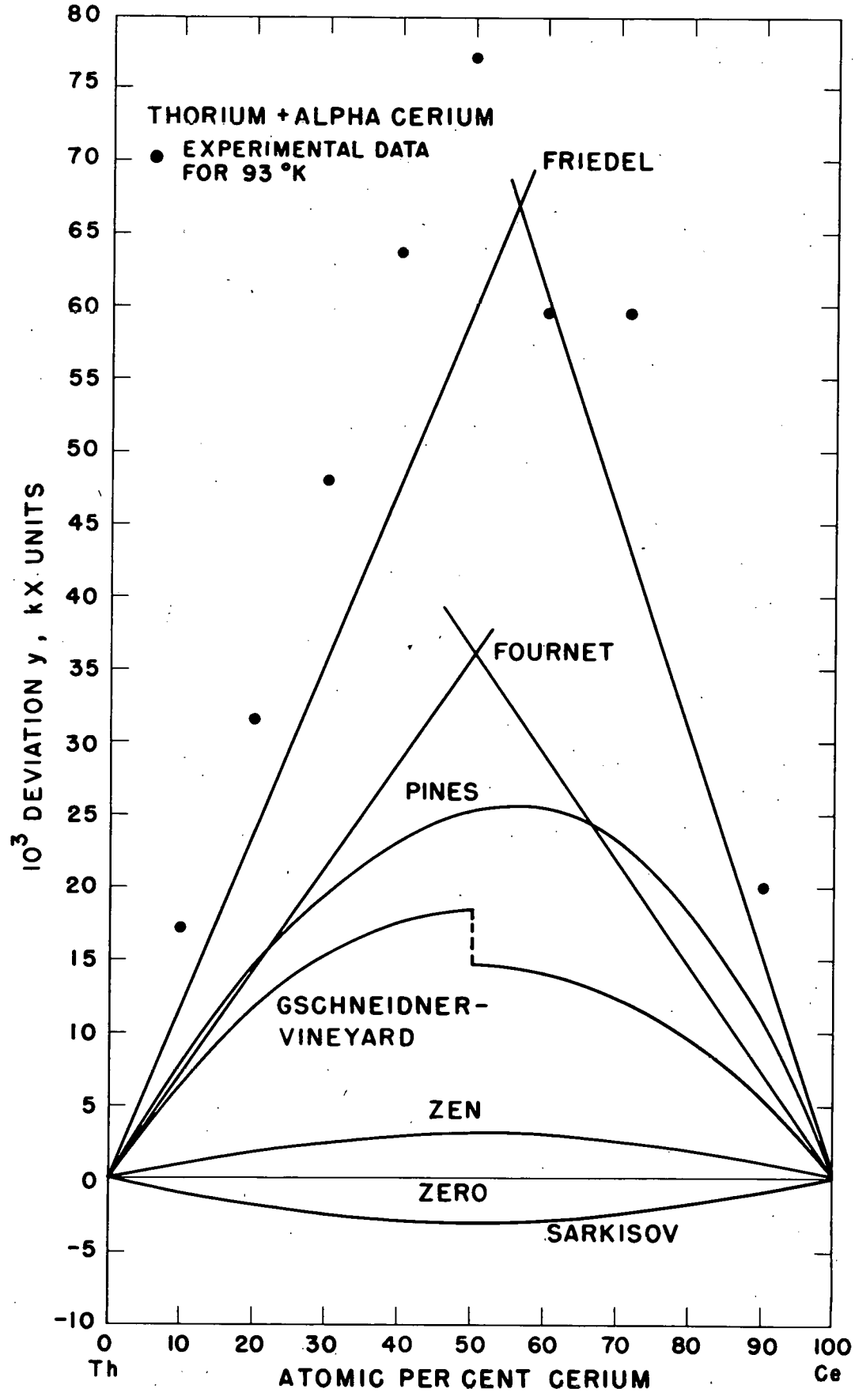
ATOMIC PER CENT CERIUM

Fig. 3. Comparison of the Observed and Computed Positive Deviations from Vegard's Law for the α phase at 93°K.


THORIUM + ALPHA CERIUM
EXPERIMENTAL DATA FOR 93 °K
FRIEDEL
FOURNET
PINES
GSCHNEIDNER-VINEYARD
ZEN
ZERO
SARKISOV
10^3 DEVIATION y, kX UNITS
ATOMIC PER CENT CERIUM
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susceptibility and electrical resistivity data of Bates and Newman[17], is consistent with this picture.

Inasmuch as Evans and Raynor[2] regarded strain energy in the solid solution as a major cause of the deviation y in the thorium-rich alloys, it was thought desirable to attempt to calculate the magnitude of y from elastic theory. The major result is illustrated in Fig. 2, namely that a large fraction of the observed deviations could be accounted for by using Friedel's analysis of strain in a solid solution. He does point out that part of the uniform dilation of the matrix is due to surface forces, as discussed by Eshelby[18]. The effectiveness of the Friedel approach is emphasized by the good agreement obtained between the observed and calculated values of y in Fig. 3.

It is interesting that Sarkisov's model, which is based on the distribution and interaction of valence electrons in a metal, leads to y values that are in very good agreement with the experimental values for γ phase alloys. Turning to the y values calculated for α solid solutions, Fig. 3 shows that the magnitude of these negative deviations is decreased when the valence, f_B, is changed from 3 to 3.62 for the γ phase. Only with f_B in the vicinity of 4 does y become positive, and then it is very small. Since assuming an increased valence for cerium would not significantly improve the agreement between observed and calculated values of y for the γ solid solutions, it is doubtful that Sarkisov's model can be used to show that the cause of the deviations is primarily of an electronic rather than of an elastic nature. The almost complete lack of agreement of y values for α solid solutions increases the doubt.

It is also doubtful that the Gschneidner-Vineyard[11] theory, which is based on second order elastic effects, can properly be used to calculate y for γ solid solutions, in view of the difference in valence between thorium and cerium. This restriction is less important for the α solid solutions. Although the calculated values of y do have the correct sign, their magnitude is too small. Perhaps it is not surprising that these second order elastic corrections are small in comparison with those obtained by using simple elastic theory as Pines, Friedel and Fournet did. Unless the term in Equation (4) becomes negative, i.e. the pressure dependence of μ becomes very small in comparison with μ/B (which is equivalent to Gruneisen's constant becoming negative), the values of y calculated with the Gschneidner-Vineyard theory cannot become negative. Presumably, negative deviations are only observed when the elements of a binary system differ in valence.

Equation (3) appears to be symmetrical under the change of subscript from A to B, i.e. with the change of identifying which element is the solvent. This is true only if the elastic term in equation (4) is obtained for the solid solution and not merely for the solvent. In the absence of data on $d\mu/dp$ for thorium and of all three numbers which appear on the left hand side of equation (3) for cerium-thorium alloys, it was necessary to calculate the values of y with the approximate value obtained from Grüneisen's constant. The break in the Gschneidner-Vineyard curve in Fig. 3 reflects the change from thorium to α cerium values at 50 a/o. This change was more difficult to depict in Fig. 2.

Because the Friedel and Fournet equations are linear in concentration C_B, two branches were used to represent the curve of y over the complete range of C_B from 0 to 1. The bracketed terms in equations (5),(6) and (7) lead to a further difficulty. This term in Fournet's expression merely changes sign when A is substituted for B, i.e. the equation is antisymmetric. The bracketed term in Equation (5) would take on an entirely different value under this substitution of A for B. Thus, although the factor $C_A C_B(\Delta d)(\Delta\chi)$ in Pines' equation would not change, the value of y would change substantially since only the shear modulus, μ_A, and not μ_B, occurs in the equation. Reference to Friedel's equation will show that the two compressibilities are present in an unsymmetric manner. Thus, y is not single valued over the whole composition range.

It is not appropriate here to discuss the differences in assumptions and approximations that lead to the four expressions for y that are based on the elastic properties of the component metals, namely Equations (3),(5),(6) and (7). Instead, the reader is referred to the original papers.

The large magnitude of the deviations found for thorium-cerium alloys presumably arises from the unusual compressibility of cerium. Thus, substantial deviations from the linear Vegard's Law might be anticipated for any cerium alloy. This idea is difficult to test because cerium does not dissolve extensively in many solvents. As a first approximation one can use the Pines-Friedel criterion P as an indication of the size of y to be anticipated in other binary systems. The values of P for several alloy systems involving

cerium and thorium are presented in Table IV.

Table IV. The Pines-Friedel Criterion, P, for Deviations from Vegard's Law.

Solute	Solvent	$Px10^7$
γ-Cerium	Thorium	-0.62
	δ-Plutonium	-3.26
	Lanthanum	-0.016
	Zirconium	-6.69
	Yttrium	-0.44
	Magnesium	-2.56
α-Cerium	Thorium	2.41
	Zirconium	-4.09
Lanthanum	Thorium	-1.82
δ-Plutonium	Thorium	0.74

In preparing this table, the Pauling radius corrected to coordination number R(CN 12) was used in place of the lattice parameters which were used in the equations above. The two values for the cerium-thorium system are repeated here for comparison. As shown in Figs. 2 and 3, the calculated value of y is negative for γ but positive for α-cerium alloyed with thorium. The values of P in Table IV are obviously in agreement.

Evans and Raynor comment that the apparent atomic diameter of plutonium in thorium suggests that plutonium takes on a lower valence, similar to that of the solvent, when dissolved in thorium, that is, the solute is induced, where possible, to take on the valence of the solvent. From P, one anticipates a positive deviation

from Vegard's Law and an apparent atomic diameter of plutonium larger than its normal value. Elastic theory thus accounts for the behavior of plutonium as well as of cerium. Unpublished research at the University of Birmingham shows that the observed y is a large negative number for cerium dissolved in zirconium, which is in agreement with the prediction from Table IV. Contrary to prediction, however, y apparently is not negative for cerium dissolved in α-yttrium. Experimental data by Gschneidner, Elliott and Prince[19] indicate that the observed y is positive and small for rare earth additions to cerium. For most of the rare earths P would be small but negative, indicating that R(CN 12) may not be a suitable measure of interatomic distance for the present purpose.

The influence of phase instability on the lattice parameter is illustrated in Fig. 1. The lattice parameter of thorium-rich alloys changes only slightly with temperature. In contrast, if one could go continuously from FCC γ to FCC α phase in unalloyed cerium, the coefficient of expansion should be very large. This will be discussed in a subsequent paper. As indicated in Table II, such a continuous change is possible if sufficient thorium (approximately 50 a/o) is alloyed with cerium. Dilatometric work by Gschneidner, Elliott and McDonald[20] confirms this idea. They suggest, on the basis of the trend of the change in the volume of transformation due to alloying, that 47 a/o thorium is sufficient to eliminate the $\gamma \rightarrow \alpha$ transformation.

At different temperatures, the deviations from Vegard's Law occur in such a way that the isothermal lattice parameter curves for the thorium-rich alloys tend to come together (see Fig. 1). This may possibly reflect the inherent instability of the solute cerium in this temperature range. Thus, at moderately high temperatures where only γ-cerium is stable, much of the deviation from Vegard's Law might be expected to disappear. However, unless the compressibility of cerium falls rapidly with increasing temperature, the Pines-Friedel criterion P would predict negative values of y over the temperature range where γ-cerium is stable.

The evidence presented here indicates that much of the observed deviation from Vegard's Law can be accounted for on the basis of elastic models. Evans and Raynor[2] showed that the observed deviations in the γ-cerium solid solutions can be associated with valence changes in the cerium when dissolved in a smaller matrix. Above the thermodynamic critical point for cerium, which is reported[3] to be 307°C, only one FCC phase can be induced at any pressure, and thus, above that temperature, the valence of cerium cannot be influenced by the solvent. Measurement of the lattice parameters above that temperature might well provide a further test of the reliability of the Friedel model for predicting y.

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CONCLUSION

Experiments with binary solid solutions containing cerium and thorium have shown that the deviations from Vegard's Law have been found to be negative at room temperature, and the observed lattice parameters agree well with those reported by Evans and Raynor. At low temperature, however, the deviations were observed to be strongly positive. Evans and Raynor have associated the large contraction in the γ-cerium phase with the promotion of a 4f electron into the valence band and suggest that this promotion is facilitated by reducing the strain in the matrix. A comparison of the values of the deviations, y, calculated by means of various models shows that the sign and magnitude of y in both the α and γ cerium phases can be accounted for by simple elastic distortion.

The Friedel elastic sphere model yielded y values in excellent agreement with those observed for α cerium solid solutions. However, the observed values for γ solutions are more negative than those calculated, suggesting that the Evans-Raynor valence mechanism plays an additional role.

The Pines-Friedel criterion for predicting the sign of y depends on the difference in compressibilities, $\Delta\chi$, and lattice spacings, Δd. In most of the other binary systems considered P gives the sign of observed deviation correctly.

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