

Form Approved
OMB No. 0704-0158

1. The report to Bureau (NY 100-101101) dated 11/11/54, estimated the average "burden" response, including the time for reviewing the entire description of the data source, preparing and submitting the data record and completing the "burden" form, as approximately 100 minutes. This estimate is based on the assumption that the respondent is a person who is familiar with the data source and the "burden" form, and that the respondent is not a member of the Bureau staff.

19960719 018

OFFICE OF NAVAL RESEARCH

Grant or Contract N00014-93-1-0904

R&T Code 3134037ess08
Scientific Officer: Dr. John Pazik

Technical Report No. 31

"Thermoelectric properties of $\text{RE}_x\text{Ce}_{1-x}\text{Pd}_3$
(RE = Y, $\text{La}_{0.5}\text{Y}_{0.5}$, Nd)"

by

Y. Ijiri and F.J. DiSalvo

Submitted to

Physical Review B

Cornell University
Department of Chemistry
Ithaca, NY 14853

July 10, 1996

Reproduction in whole or in part is permitted for any purpose
of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

Thermoelectric properties of $\text{RE}_x\text{Ce}_{1-x}\text{Pd}_3$ ($\text{RE} = \text{Y}, \text{La}_{0.5}\text{Y}_{0.5}, \text{Nd}$)

Y. Ijiri* and F.J. DiSalvo

*Baker Laboratories, Department of Chemistry,**Cornell University, Ithaca, NY 14853*

The intermediate valent compound CePd_3 has an unusually large thermoelectric power (from 100-300 K), which is interesting from the perspective of thermoelectric cooling devices. To optimize the thermoelectric properties, we have investigated rare earth substituted samples of the form $\text{RE}_x\text{Ce}_{1-x}\text{Pd}_3$ where $\text{RE} = \text{Y}, \text{La}_{0.5}\text{Y}_{0.5}$, and Nd . We have found that the intermediate valent state is highly dependent on the nature of the rare earth dopant and in particular to any local strains or bond distance changes. With Nd dilution, a small enhancement of the thermoelectric power factor α^2/ρ is observed.

PACS: 72.15.Eb, 72.15.Jf, 75.30.Mb

*Present address: National Institute of Standards and Technology,
Gaithersburg, MD 20899

I. INTRODUCTION

Recently, there has been a renewed interest in finding better materials for thermoelectric cooling devices.¹ The efficiency of such devices is determined by the materials' transport properties and is maximized for large values of the figure of merit Z

$$Z = \alpha^2 / \rho \kappa \quad (1)$$

where α is thermoelectric power or Seebeck coefficient, ρ is the electrical resistivity, and κ is the thermal conductivity.

As has been suggested by Gambino² and more recently by Mahan,³ one potential source of new thermoelectric materials is a class of rare earth intermetallic compounds, known as intermediate valence compounds. In these materials, the interaction of the f electron with the conduction electrons leads to a sharp feature in the density of states at the Fermi level which results in unusually large values of the thermoelectric power (50-100 $\mu\text{V/K}$) in the temperature range from ≈ 100 -300 K. While the electrical resistivity and thermal conductivity show anomalous temperature dependencies as well, the overall scale is more similar to other rare earth intermetallics, leading to relatively large values of Z for this class of compounds. For example, the intermediate valent compound CePd_3 has a figure of merit Z of ≈ 0.5 - $1.0 \times 10^{-3} \text{ K}^{-1}$ (Ref. 2, 4-5) in comparison to the 2 - $3 \times 10^{-3} \text{ K}^{-1}$ of currently-used Bi_2Te_3 based materials.⁶

In order to assess the potential of such intermetallics for thermoelectric cooling applications, we have investigated in more detail the sensitivity of the intermediate valent state to chemical substitution on the rare earth site in CePd_3 . While substantial work has already been done to characterize the effect of simple substitutions on intermediate valence,⁷ it is often unclear exactly what are the critical factors in such cases. For instance, in the $\text{Y}_x\text{Ce}_{1-x}\text{Pd}_3$ system,⁸ upon substitution, the overall lattice parameter decreases with increasing x , thus decreasing both the average RE-RE and RE-Pd bond distances. The local distribution of bond distances of Ce-Ce and Ce-Pd may also be affected on alloying with YPd_3 . The coherence of the Ce lattice is also destroyed, as the Y occupies Ce sites at random. The overall valence electron count is decreased as x increases, since in CePd_3 , the f electron is not completely localized, and therefore this material has slightly more "free" electrons than YPd_3 . As will be addressed later, there is finally an issue of the sample homogeneity for these alloyed systems.

In addition to increasing our understanding of the factors regulating intermediate valence, the rare earth diluted CePd_3 samples are of specific interest from the perspective of optimizing thermoelectric materials. For these intermediate valent systems, the magnitude of the electrical resistivity is very sensitive to the Ce concentration, while the magnitude of the thermopower is less so. In the simplest sense, we can understand the concentration dependencies of the resistivity and thermopower by adapting Matthiessen's rule and the Nordheim-Gorter rule, respectively to consider

two scattering mechanisms, one Kondo or f electron related and the second due to normal lattice contributions.⁹ Explicitly, then,

$$\rho(c) = \rho_{Kondo} + \rho_{lattice} = (1-x)\rho_{Kondo}^0 + \rho_{lattice} \quad (2)$$

$$\text{and } \alpha_{total} = \frac{\alpha_{Kondo}\rho_{Kondo} + \alpha_{lattice}\rho_{lattice}}{\rho_{Kondo} + \rho_{lattice}} \quad (3)$$

where ρ_{Kondo}^0 is f electron part of the resistivity in the pure Ce intermediate valence material and $0 \leq x \leq 1$. On the basis of Eq. (2-3) and the measured resistivity and thermopower of the end members, the expected concentration dependence of $RE_xCe_{1-x}Pd_3$ can be computed as shown in Fig. 1. Hence by diluting the Ce concentration, if the intermediate valence state is maintained, it is expected that the thermopower can remain relatively high, while the electrical resistivity drops with concentration. It is less clear how the thermal conductivity will behave on decreasing the Ce concentration, but the phonon contribution should be reduced due to the disorder on the rare earth site. The thermoelectric figure of merit, $Z = \alpha^2/\rho\kappa$, then should increase on Ce dilution if the intermediate valence state still exists with the same characteristic features in the 100-300 K temperature range.

Thus in this work, we report the effects of rare earth substitution in three specific systems: 1) $Nd_xCe_{1-x}Pd_3$, 2) $(La_{0.5}Y_{0.5})_xCe_{1-x}Pd_3$, and again, 3) $Y_xCe_{1-x}Pd_3$. By looking at systems with average lattice parameters that are similar (Nd, La/Y) and different (Y) to $CePd_3$, we will examine in more detail the factors governing the intermediate valence state and potential uses in thermoelectric devices.

II. SAMPLE PREPARATION AND CHARACTERIZATION

The polycrystalline samples were synthesized by arc-melting stoichiometric amounts of the elements (all of purity > 99.9%) in a water-cooled Ta-coated copper hearth under a flow of Ti-gettered Ar (Centorr Furnaces, model 2B-20). The arc-melted beads were flipped over and remelted four to five times to increase homogeneity.

The samples were then annealed in conditions listed in Table I. To suppress Pd vaporization, the samples were sealed under Ar in Ta tubing. For annealing temperatures below 1300-1350 °C, the Ta ampoules were then placed in an alumina tube under Ar and heated in a Pt furnace. For higher temperatures, the Ta ampoules were suspended in an evacuated quartz tube and heated inductively in an RF furnace (Ameritherm, Model SP 2.5).

The sample quality was assessed by electron microprobe analysis (JEOL 733 Superprobe) and powder X-ray diffraction (Scintag XDS 2000 powder diffractometer). As expected on the basis of microprobe work on the $Y_{1-x}U_xPd_3$ system,¹⁰ the annealing conditions were critical for achieving macroscopic homogeneity in the alloy samples, as compared to the end members, $CePd_3$ and YPd_3 . For example, an unannealed sample of $(La_{0.5}Y_{0.5})_{0.8}Ce_{0.2}Pd_3$ showed Y concentrations varying from 2 to 12% at different parts of the bead in contrast to the expected 10% based on stoichiometry. Also, the full widths at half maximum (FWHM) of the X-ray diffraction peaks were greater than 0.5° in 2θ , indicating the inhomogeneous nature of the samples. Annealing at

close to the solidus temperature led to single-phase, sharp diffraction patterns ($\approx 0.2^\circ$ on average) and observed concentration variations of less than 1-2%, at the limit of error for standardless microprobe analysis. Proximity to the solidus temperature for annealing was of considerable importance, as a one month anneal of $\text{La}_{0.5}\text{Y}_{0.5}\text{Pd}_3$ at 1200°C still resulted in broad X-ray diffraction peaks ($\approx 0.5^\circ$ FWHM). In this regard, the samples were annealed at as close to the solidus temperature as possible ($100^\circ\text{C} \pm 50^\circ\text{C}$) without significant Pd vaporization which becomes substantial for $> 1400^\circ\text{C}$. The total mass losses due to arc melting and annealing the samples were all less than $0.5\% \pm 0.2\%$. The lattice parameters of the end members (CePd_3 , $\text{La}_{0.5}\text{Y}_{0.5}\text{Pd}_3$, NdPd_3 , and YPd_3) are listed in Table II and agree well with those in the literature.¹¹ While the $\text{Y}_x\text{Ce}_{1-x}\text{Pd}_3$ lattice parameters decrease significantly as x is increased,⁸ those of the other two systems ($(\text{La}_{0.5}\text{Y}_{0.5})_x\text{Ce}_{1-x}\text{Pd}_3$ and $\text{Nd}_x\text{Ce}_{1-x}\text{Pd}_3$) remain constant within error.

After all annealing treatments were completed, the samples were cut into rectangular bars using a string saw with a diamond-impregnated blade. The thermoelectric power was measured using a home-built apparatus¹² in which a small, steady temperature gradient ($\approx 0.5 - 1.5\text{ K}$) was placed across the sample, and the resulting voltage measured, subtracting the known thermopower of the wires. The electrical resistivity was measured using standard four-probe AC techniques (Stanford Research Systems lock-in amplifiers). Absolute resistivity values were determined using the sample dimensions and comparing to a known metal standard of similar size.

III. RESULTS AND DISCUSSION

In Fig. 1, we plot the room temperature values of the thermopower as a function of doping concentration x for the $Y_xCe_{1-x}Pd_3$, the $(La_{0.5}Y_{0.5})_xCe_{1-x}Pd_3$, and the $Nd_xCe_{1-x}Pd_3$ systems. Also shown on the figure is the expected concentration behavior of the thermopower based on the Nordheim-Gorter rule (Eq. 3) using the measured resistivity and the measured thermopower of the end members. Note that the concentration dependence of the thermopower varies substantially for the three different diluting rare earth species. While in all three cases the thermopower decreases with increasing x , the $Y_xCe_{1-x}Pd_3$ thermopower decreases faster than the other two, in good agreement with previously published results.⁴ In contrast, for the $Nd_xCe_{1-x}Pd_3$ system, the thermopower remains very high even with as much as 40% doping with Nd. The $(La_{0.5}Y_{0.5})_xCe_{1-x}Pd_3$ samples display behavior intermediate to these two other systems. Note as well that while the $Y_xCe_{1-x}Pd_3$ system deviates significantly from the Nordheim-Gorter model, the $Nd_xCe_{1-x}Pd_3$ system follows the predictions reasonably well to $\approx 40\%$ doping.

These results indicate that the nature of the rare earth doping species has a dramatic effect on the intermediate valence state. The simplest picture in which the state depends only on the Pd atoms surrounding each Ce cannot be accurate, in that the Pd lattice remains the same in all three doping systems with substantially different results. While in the case of the Ce-Y system, the

large changes in overall lattice parameter will also distort the Ce-Pd distances, this effect should not be as important in the Ce-La/Y and Ce-Nd systems in which the rare earth metals are much better matched in size. Clearly, more than the nearest neighbor Ce-Pd interactions are important in determining the details of the intermediate valence state. CePd_3 also appears to be sensitive to local strains as evidenced by the differences in the $(\text{La,Y})_x\text{Ce}_{1-x}\text{Pd}_3$ and $\text{Nd}_x\text{Ce}_{1-x}\text{Pd}_3$ systems. Constant average Ce-RE distances (as determined by X-ray diffraction) in the Ce-La/Y system do not seem to give equivalent thermoelectric effects to the locally matched Ce-RE distances of the Ce-Nd system.

On the other hand, the closer similarity of the $\text{Nd}_x\text{Ce}_{1-x}\text{Pd}_3$ system to the simple Nordheim-Gorter prediction (at least for $x \leq 0.4$) suggests that if factors like local bond distances are carefully controlled, the concentration dependence may vary in a manner very similar to such a model. The deviations observed here for concentrations $x > 40\%$ may indicate the role of the coherence of the lattice, as the Nd atoms, with different 4f and 5d energy levels relative to Ce, disrupt the electronic coherence of the Ce atoms. The overlap between Ce d states and the corresponding Nd d states may not be as effective due to their energy differences. Changes in the crystal field of the Ce site are well-known to modify transport properties such as the thermopower.¹³ Alternatively, the deviations at higher concentrations may stem from small differences in valence electron count, as the Nd is purely trivalent unlike the Ce with its partial f electron delocalization.

Given the elevated thermopower values for the Nd-doped samples, we were interested in exploring the properties in more detail. In Fig. 2, we plot the electrical resistivity of the $\text{Nd}_x\text{Ce}_{1-x}\text{Pd}_3$ samples as a function of temperature for the range of 4-295 K. With Nd doping, the low temperature peak structure of CePd_3 is suppressed, but in addition, the overall scale of the electrical resistivity is decreased.

The sensitivity of the resistivity peak to chemical modification has been observed in a variety of other doping experiments and is thus not surprising in this context.^{5, 14} In contrast to these large deviations from Matthiessen's rule at low temperature, we note that the high temperature behavior of the samples is much less anomalous. Table III lists the observed room temperature resistivity values in comparison to those expected from a simple linear scaling with concentration as described by Matthiessen's rule. Note the reasonable agreement between the two sets of values. The electrical resistivity and thermopower results suggest that at least at room temperature, the concentration dependence of intermediate valence in the $\text{Nd}_x\text{Ce}_{1-x}\text{Pd}_3$ system can be described to a certain extent by relatively simple models.

While the Nd results are encouraging, we note that as shown in Fig. 3, the measured thermoelectric power factor α^2/ρ maximizes at only 1.25 times that of CePd_3 for $x = 0.4$. Assuming no change in the thermal conductivity at this concentration, we obtain a figure of merit Z that is still lower than the $\approx 2.3 \times 10^{-3} \text{ K}^{-1}$ of Bi_2Te_3 , although, the thermal conductivity must be measured to definitely determine Z .

IV. CONCLUSION

In summary, the results of investigating the thermopower and resistivity of $\text{RE}_x\text{Ce}_{1-x}\text{Pd}_3$ systems clearly indicate the importance of the rare earth site in maintaining the intermediate valence state. While this sensitivity to chemical substitution is expected on the basis of previous simple doping experiments, we note that some systematics can be found in the three rare earth systems studied here. It appears that by carefully controlling the local strains and bond distances, we can maintain the intermediate valence nature of CePd_3 to as much as 40% dilution with NdPd_3 . In systems with more variability in these parameters (i.e. the La/Y and Y systems), the large thermopower values are diminished more quickly. For Nd substitution with $x > 40\%$, the deviations in α from simple model predictions may indicate the role of the disruption of the lattice coherence, the change in energy levels, or the small decreases in valence electron count on substitution. These results illustrate the delicate nature of the intermediate valence state and underscore the challenges in finding a better thermoelectric material in this class of compounds.

ACKNOWLEDGMENTS

We would like to thank D.L. Cox for useful discussions regarding this project. This work was supported by the Office of Naval Research. Y.I. acknowledges support as well from a National Physical Science Consortium Fellowship.

REFERENCES

- ¹C. Wood, Rep. Prog. Phys. **51**, 459 (1988); T. Caillat, A. Borshchevsky, and J.-P. Fleurial, *Proceedings of the XIth International Conference on Thermoelectrics, University of Texas at Arlington, 1992*, edited by K.R. Rao (University of Texas at Arlington Press, Arlington, 1993), p. 98; L.D. Hicks and M.S. Dresselhaus, Phys. Rev. B **47**, 12727 (1993).
- ²R.J. Gambino, W.D. Grobman, and A.M. Toxen, Appl. Phys. Lett. **22**, 596 (1973).
- ³G.D. Mahan, Bull. Am. Phys. Soc. **41**, 58 (1996).
- ⁴D. Jaccard, M.J. Besnus, and J.P. Kappler, J. Magn. Magn. Mater. **63&64**, 572 (1987).
- ⁵H. Schneider and D. Wohlleben, Z. Phys. B **44**, 193 (1981).
- ⁶M.V. Vedernikov, in *Intermetallic Compounds: Principles and Practice*, edited by J.H. Westbrook and R.L. Fleischer (John Wiley, Chichester, 1995), Chap. 20.
- ⁷V.U.S. Rao, R.D. Hutchens, and J.E. Greedan, J. Phys. Chem. Solids **32**, 2755 (1971); H. Stiou, D. Jaccard, and J. Sierro, in *Valence Instabilities*, edited by P. Wachter and H. Boppart (North-Holland Publishing, Amsterdam, 1982), p. 443; Selim and T. Mihalisin, Solid State Comm. **59**, 785 (1986); P.A. Veenhuizen, Yang Fu-ming, H. van Nassou, and F.R. deBoer, J. Magn. Magn. Mater. **63&64**, 567 (1987).

-
- ⁸J.P. Kappler, G. Krill, M.J. Besnus, M.F. Ravet, N. Hamdaoui, and A. Meyer, J. Appl. Phys. **53**, 2152 (1982).
- ⁹R.D. Barnard, *Thermoelectricity in Metals and Alloys*, (Taylor and Francis, London, 1972).
- ¹⁰S. Süllo, T.J. Gortenmulder, G.J. Nieuwenhuys, A.A. Menovsky, and J.A. Mydosh, J. Alloys Compd. **215**, 333 (1994); J. Xu, P.J.C. Signore, B. Andraka, W.A. Acree, M.W. Meisel, and Y. Takano, J. Alloys Compd. **216**, 33 (1994).
- ¹¹P. Villars and L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (ASM International, Materials Park, 1991).
- ¹²R.A. Gordon, Ph.D. thesis, Cornell University, 1995.
- ¹³B. Cornut and B. Coqblin, *Phys Rev. B* **5**, 4541 (1972); B. Wittershagen and D. Wohlleben, *J. Magn. Magn. Mater.* **47&48**, 497 (1985); S.M.M. Evans, A.K. Bhattacharjee, and B. Coqblin, *Physica B* **171**, 293 (1991).
- ¹⁴M.J. Besnus, J.P. Kappler, and A. Meyer, J. Phys. F **13**, 597 (1983).

TABLE I. Annealing conditions for $\text{RE}_x\text{Ce}_{1-x}\text{Pd}_3$ samples used for subsequent characterization or property measurements.

x	RE	Temperature, time of anneal	Furnace for annealing
0.0 ^a	--	unannealed; 1200 °C, 1 day	Pt
0.2	Nd	1225 °C, 1 day	Pt
0.4	Nd	≈1300 °C, 1 day	RF
0.6	Nd	1350 °C, 1 day	Pt
0.8	Nd	≈1350 °C, 1 day	RF
1.0	Nd	1350 °C, 1 day	Pt
0.2	La/Y	1250 °C, 1 day	Pt
0.4	La/Y	1300 °C, 1 day	Pt
0.6	La/Y	1350 °C, 1 day	Pt
0.8 ^b	La/Y	unannealed; ≈1400 °C, 1 day	RF
1.0 ^b	La/Y	1200 °C, 1 month; ≈1400 °C, 1 day	conventional RF
0.2	Y	1300 °C, 1 day	Pt
0.4	Y	1300, 1350 °C, 1 day	Pt
0.6	Y	1350 °C, 1 day	Pt
0.8	Y	≈1400 °C, 1 day	RF
1.0 ^a	Y	unannealed; ≈1400 °C, 1 day	RF

^aNon-alloy samples.

^bSample conditions discussed in Section II.

TABLE II. Lattice parameters of REPd₃ samples and relevant values from literature.

Material	Lattice parameter (Å)	Literature value (Å)
CePd ₃	4.126 ± 0.003 ^a	4.112-4.128
NdPd ₃	4.129	4.120-4.130
La _{0.5} Y _{0.5} Pd ₃	4.124	-----
YPd ₃	4.074	4.061-4.076

^aError reflects both instrumental uncertainty and uncertainty from measuring different samples of nominally same stoichiometry.

TABLE III. Measured room temperature resistivity values for $\text{Nd}_x\text{Ce}_{1-x}\text{Pd}_3$ as well as predicted values based on Matthiessen's rule and the end member values ($x = 0, 1.0$).

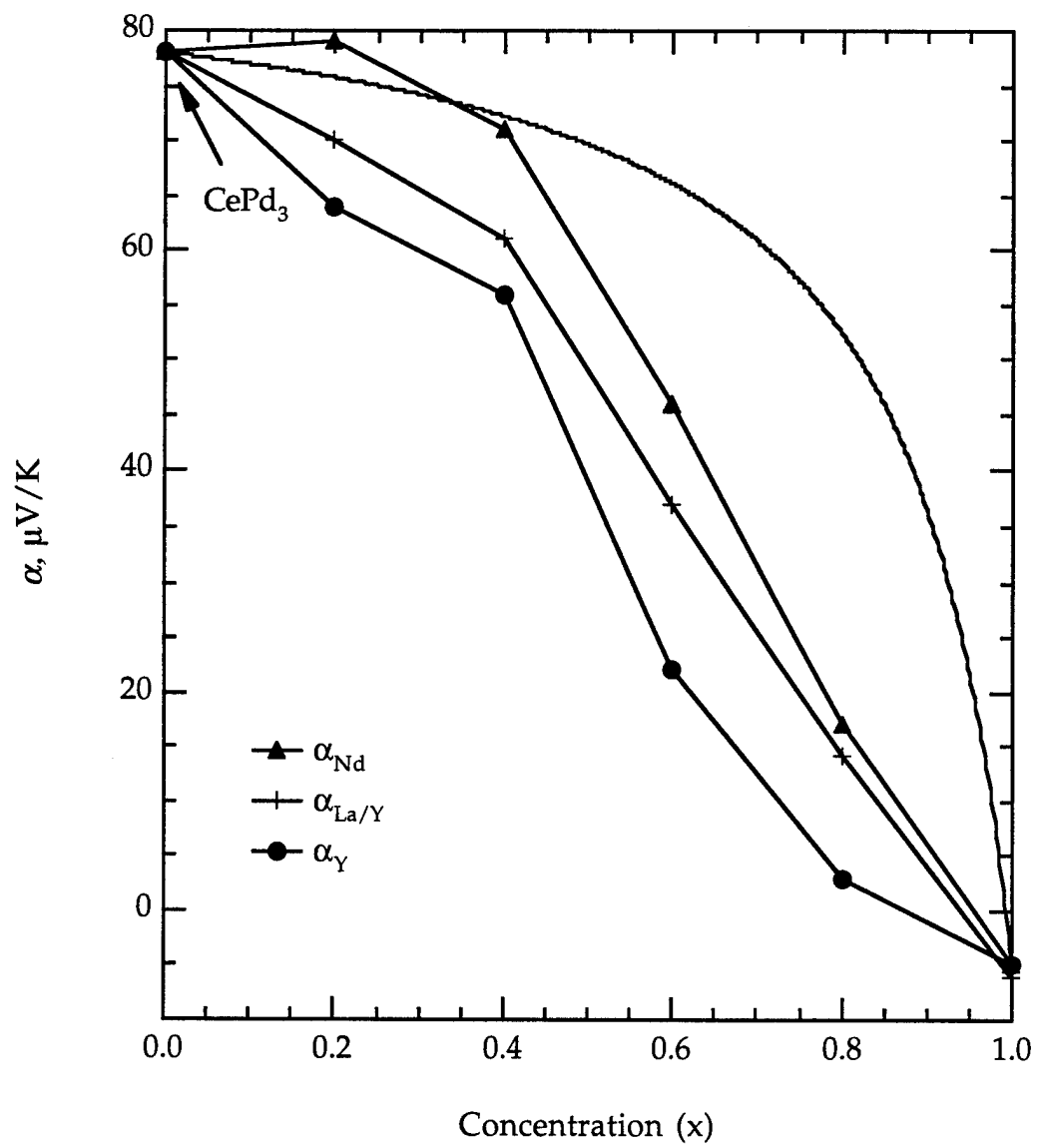
Concentration x	Measured ρ , $\mu\Omega\text{-cm}$	Predicted ρ , $\mu\Omega\text{-cm}$
0.0	117	---
0.2	100	96
0.4	76	75
0.6	46	55
0.8	28	34
1.0	13	---

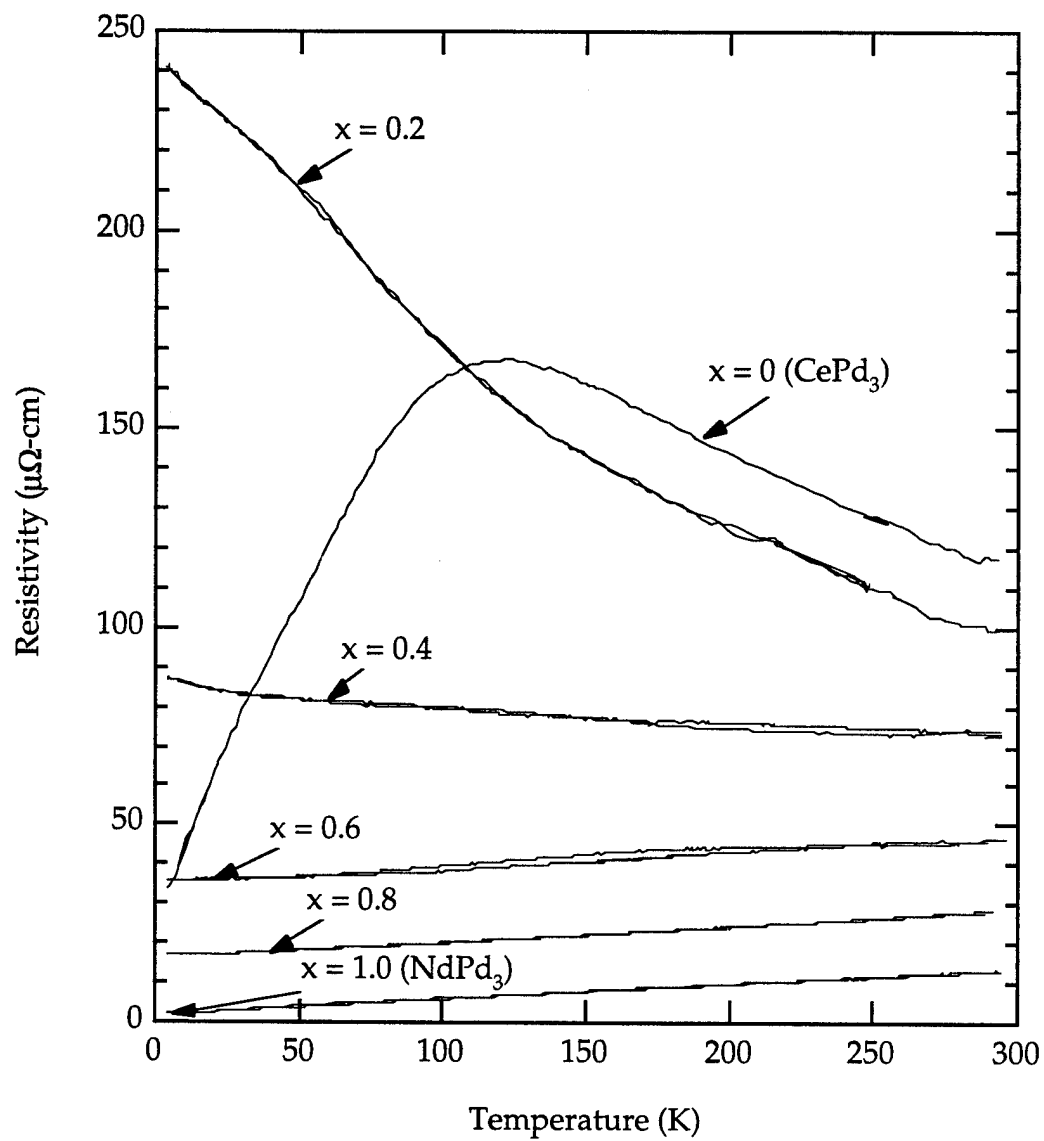
LIST OF FIGURE CAPTIONS

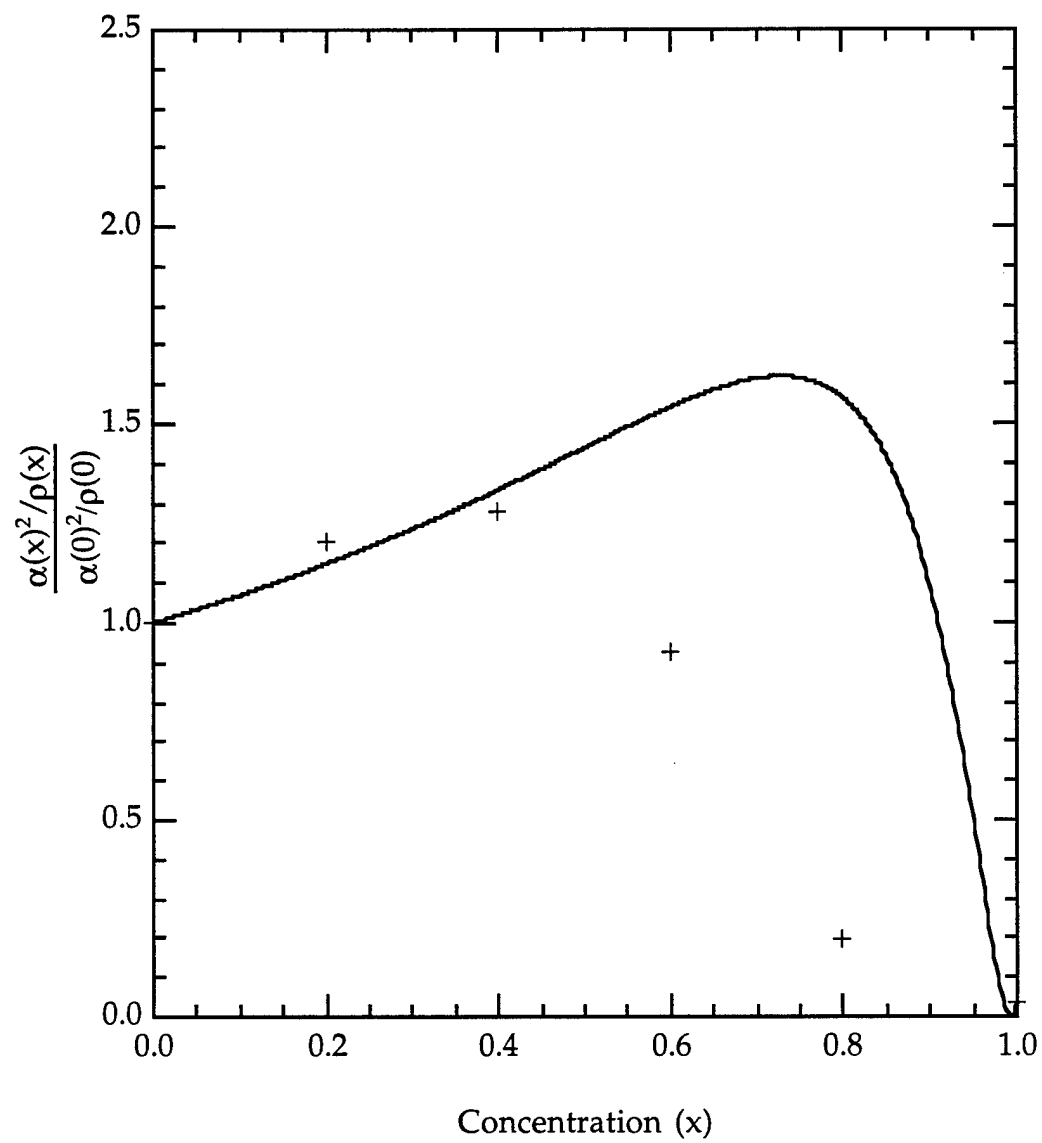
FIG. 1. Thermoelectric power vs. concentration for doping with Nd, La/Y, and Y in $\text{RE}_x\text{Ce}_{1-x}\text{Pd}_3$. Shown as a solid line with no data points is the expected dependence on the basis of Nordheim-Gorter rule.

FIG. 2. Electrical resistivity ρ of $\text{Nd}_x\text{Ce}_{1-x}\text{Pd}_3$ from 4-295 K.

FIG. 3. α^2/ρ for $\text{Nd}_x\text{Ce}_{1-x}\text{Pd}_3$ as a function of concentration x . Shown as a solid line is the expected dependence on the basis of Matthiessen's rule and the Nordheim-Gorter rule.







Technical Report Distribution List

Dr. John C. Pazik (1)*
Physical S&T Division - ONR 331
Office of Naval Research

800 N. Quincy St.
Arlington, VA 22217-5660

Defense Technical Information
Ctr (2)
Building 5, Cameron Station
Alexandria, VA 22314

Chemistry Division, Code 385
NAWCWD - China Lake
China Lake, CA 93555-6001

Dr. James S. Murday
(1)
Chemistry Division, NRL 6100
Naval Research Laboratory
Washington, DC 20375-5660

Dr. Peter Seligman (1)
NCCOSC - NRAD
San Diego, CA 92152-5000

Dr. John Fischer (1)

Dr. Bernard E. Douda (1)
Crane Division
NAWC
Crane, Indiana 47522-5000

* Number of copies required