REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE June 1, 1995

3. REPORT TYPE AND DATES COVERED Tech Rpt. # 24

4. TITLE AND SUBTITLE
Magnetic and Electrical Properties of the Substitution Series in $Ce_2Ni_{2x}Pd_{2(1-x)}In$

5. FUNDING NUMBERS
N00014-93-1-0904
Dr. John Pazik
R&T: 3134037ess08

6. AUTHOR(S)
Y. Ijiri and F.J. DiSalvo

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry
Cornell University
Ithaca, NY 14853-1301

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
Chemistry Program
800 N. Quincy St.
Alexandria, VA 22217

DTIC
SELECTE
JUN 28 1995
S D
B

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
This document has been approved for public release and sale; its distribution is unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The magnetic susceptibility and the electrical resistivity of $Ce_2Ni_{2x}Pd_{2(1-x)}In$ are studied for $x = 0.0$ to 1.0. The magnetic properties change continuously from the ferromagnetic Ce_2Pd_2In with a T_c near 4 K to the temperature independent paramagnet Ce_2Ni_2In. The electrical resistivity varies systematically from hysteretic in the brittle Ce_2Pd_2In to simple metal-like in Ce_2Ni_2In. The property changes are discussed in terms of lattice and concentration effects.

14. SUBJECT TERMS
cerium intermetallics, electrical resistivity, magnetic susceptibility

15. NUMBER OF PAGES 20

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified

20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

19950626 052

OFFICE OF NAVAL RESEARCH

Grant or Contract N00014-93-1-0904

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

Technical Report No. 24

"Magnetic and Electrical Properties of the Substitution Series in $Ce_2Ni_{2x}Pd_{2(1-x)}In$"

by

Y. Ijiri and F.J. DiSalvo

Submitted to

J. Alloys and Compounds

Cornell University
Department of Chemistry
Ithaca, NY 14853

June 1, 1995

Magnetic and electrical properties of the substitution series in $Ce_2Ni_{2x}Pd_{2(1-x)}In$

Y. Ijiri and F.J. DiSalvo

Department of Chemistry, Cornell University, Ithaca, New York 14853

Abstract:

The magnetic susceptibility and the electrical resistivity of $Ce_2Ni_{2x}Pd_{2(1-x)}In$ are studied for x= 0.0 to 1.0. The magnetic properties change continuously from the ferromagnetic Ce_2Pd_2In with a T_c near 4 K to the temperature independent paramagnet Ce_2Ni_2In. The electrical resistivity varies systematically from hysteretic in the brittle Ce_2Pd_2In to simple metal-like in Ce_2Ni_2In. The property changes are discussed in terms of lattice and concentration effects.

Keywords: cerium intermetallics, electrical resistivity, magnetic susceptibility.

1. Introduction

Ternary rare earth intermetallics of the form RE_2M_2X have been the subject of much recent research [1-7]. In particular, several of the uranium-containing versions have shown unusual transport properties associated with Kondo effects [5-7]. Ce_2Ni_2Sn also has shown significant f electron-conduction electron interactions [2] leading to an antiferromagnetically ordered Kondo system.

In a recent work, we presented the magnetic properties of the isostructural compounds Ce_2Pd_2In and Ce_2Ni_2In [1]. Ce_2Pd_2In was found to be a ferromagnet with a T_c near 4.2 K. The Ce moment of 2.48 μ_B, derived from a Curie-Weiss fit of the data, was consistent with the calculated value of 2.54 μ_B for Ce^{+3}. In Ce_2Ni_2In, the Ce moment was considerably diminished, and the susceptibility was only weakly temperature dependent. The apparent "Ce^{+4}" moment may be evidence of a Kondo-like interaction with T_K well above room temperature. Alternatively, the lack of a moment may indicate considerable hybridization of the f electrons with the conduction electrons.

Given the different properties of the isostructural end members, we were interested in exploring the crossover from the apparently localized moments to the essentially quenched ones. We anticipated that at some concentration, Kondo-like or intermediate valence properties might be observed. Thus, in this paper, we have studied the substitution series of $Ce_2Ni_{2x}Pd_{2(1-x)}In$, examining changes in lattice parameters, magnetic susceptibility, and electrical resistivity.

2. Experimental details

Samples were synthesized by arc-melting stoichiometric amounts of the elements on 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 repeatedly to increase homogeneity. Mass losses after arc-melting were less than 0.5%. The elements used in the samples were all at least of purity 99.9%. The cerium was further purified by vacuum melting into a water-cooled copper cup, leaving behind much of the outer oxide coat often present on Ce pieces. The arc-melted beads were then placed in tantalum tubing and sealed in quartz under vacuum. The samples were annealed for four weeks at 700 °C. Despite annealing, the samples had some macroscopic cracks on the surface.

Powder X-ray diffraction data on the annealed samples were taken using a Scintag XDS 2000 diffractometer with Cu K_α radiation. The patterns were analyzed using the indexing program TREOR [8] as well as a least squares lattice parameter program, Latcon-Z. The magnetic susceptibility of the samples was measured using a Faraday balance on coarsely ground, loose powder. The field dependence of the susceptibility at room temperature from 2.1 kG to 14.6 kG showed variations of less than 2%, indicating few ferromagnetic impurities. Temperature dependent data from 4.2 to 320 K were collected in a fields of 10 kG. Platinum was used as a calibration standard. The measured room temperature susceptibility of the Pt (χ(290 K)) was 1.034 x 10^{-6} emu/g, in good agreement with a literature value of 1.035 x 10^{-6} emu/g [9]. Electrical resistivity was measured using standard four probe AC techniques. Due to cracks in the samples, accurate cross-sectional area values could not be measured, and thus only relative resistivities are presented.

3. Results and discussion

3.1 Structural Data

The X-ray powder diffraction patterns for the $Ce_2Ni_{2x}Pd_{2(1-x)}In$ samples were all indexed to tetragonal cells using TREOR [8] and a least squares lattice parameter refinement program. The peak locations and major peak intensities were all consistent with those expected for materials in the U_3Si_2 structure type (space group P4/mbm). Some deviations from calculated intensities were observed for the less intense lines. These differences were expected since the powder samples were not carefully ground to the ≈ 10 μm size necessary to produce peak intensities with only small statistical deviations from the calculated random powder approximation [10].

The lattice parameters thus derived are given in Table 1 and displayed in Fig. 1. The dashed lines in the figure indicate the lattice constants expected on the basis of the x=0.0 to 0.5 samples. Note that the *a* parameter varies almost linearly upon substitution of Ni for Pd, while the *c* parameter shows a more anomalous change in slope across the substitution range. At the x=1.0

end, the deviation from the dashed lattice constant value in a ($\Delta a/a$) is only 0.5%, whereas for the c axis parameter, this deviation ($\Delta c/c$) is 2.4%.

These results are consistent with those observed in isostructural materials. In particular, for the U_2T_2M compounds, it was found that the a parameter varied linearly with the size of the transition metal element, whereas the c parameter did not vary solely on the basis of steric effects [6]. Instead, the c parameter seemed to reflect changes in electronic structure. The change in c observed here, then, suggests a difference in the nature of rare earth electronic state across the substitution series.

3.2 Magnetic Properties

Fig. 2 shows the magnetic susceptibility and inverse susceptibility for $Ce_2Ni_{2x}Pd_{2(1-x)}In$ upon heating from 4.2 K to 320K. The susceptibility data on cooling showed some discontinuities, resulting in hysteretic-like behavior. The most pronounced effect is seen in the Pd rich samples, as illustrated in Fig. 3. These discontinuities stem from the reorientation of the loose powder in the magnetic field. In non-cubic systems, crystal field effects can cause anisotropic magnetic moments, such as has been observed in $CeCoGe_3$ [11]. With significant anisotropy, the powder sample can experience a torque in the magnetic field, causing the particles to move.

Note that the heating data does not show such discontinuities, indicating a constant orientation. However, the applied field may not have been strong enough to completely orient each crystallite, since many are agglomerated with polycrystalline grains. Thus, from the heating data, we can extract moments corresponding only roughly to the strongest moment directions.

More specifically, the heating data were fit to the Curie-Weiss law:

$$\chi = \chi_0 + \frac{C}{T-\theta} \quad . \qquad (1)$$

The fit parameters were found by choosing a temperature range of fit, fixing θ, and then determining C and χ_0 using standard analysis techniques [12]. θ was varied, and for each choice, a fractional variance σ

$$\sigma = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{\chi_i - \chi_o - \dfrac{C}{T_i-\theta}}{\chi_i}\right)^2 \qquad (2)$$

was calculated. The final parameters were chosen to minimize σ over the largest temperature range.

Table 2 lists the fitting results for x=0 to 0.5 for a temperature range of 100-320 K. Below 100 K, crystal field effects and exchange interactions cause deviations from Curie-Weiss behavior. Note that for these compositions, the extracted Ce moment stays constant at a value close to the calculated 2.54 μ_B expected for Ce^{+3} moments. Thus, from the undiluted Ce_2Pd_2In to $Ce_2PdNiIn$, the major change is in θ, which goes from a ferromagnetic value of 20 K to an antiferromagnetic 39 K.

The susceptibility data for x > 0.5 deviate increasingly from the Curie-Weiss law and could not fit to Eq. (1) over a reasonable temperature range.

For the x=0.625 sample, for instance, the fitted value of θ lies within the temperature range of the fit. Since the Curie-Weiss approximation is expected to deviate as T approaches θ, it is questionable to use a temperature range which *includes* the fit value of θ.

For these high Ni content samples, the magnitude and the slope of the susceptibility vs. temperature have decreased with increasing Ni concentration x. For the x=0.75 and x=1 samples, a small amount of oxygen gas freezing in the Faraday system produced the anomalies seen at $\approx$ 50 K. The upturns below 50 K are probably due to paramagnetic impurities in the samples.

Note that the susceptibility data are consistent with the changes observed in the lattice constants. For x=0 to 0.5, the *c* axis change is only that which would be expected for the size change from Pd to Ni. This size change would likely affect the RKKY interactions and lead to the susceptibility changes observed in the exchange constant θ. For x>0.5, the *c* axis lattice parameter decreases faster, suggesting some other change in the rare earth electronic state. The susceptibility data for x>0.5 show a smooth change of Ce to a non-magnetic state at x=1.0. Taken together, the magnetic and lattice parameter data suggest a change from "Ce^{+3}" to "Ce^{+4}".

3.3 Electrical Properties

Figs. 4 a) and b) show the resistivity data for $Ce_2Ni_{2x}Pd_{2(1-x)}In$ from 4.2 K to 300 K, scaled to the 300 K values. The samples showed signs of cracking and thus, absolute values of the resistivity could not be calculated reliably from sample dimensions. The cracking was most severe in the Pd rich samples, resulting in a hysteretic curve in Fig. 4b) for Ce_2Pd_2In. This sample continued to crack upon cooling below room temperature.

Excluding the non-reproducible behavior of Ce_2Pd_2In, we see a smooth trend in the resistivity data towards simple metal-like properties in Ce_2Ni_2In. Note that we do not observe any of the signatures of a Kondo effect, as the resistivity decreases monotonically with temperature. Instead, the resistivity changes may reflect the loss of moment upon substitution, resulting in less moment-induced scattering.

The resistivity data, combined with the lack of anomalous shapes in the susceptibility data and the nearly constant Ce moment up to x=0.5, suggest that the substitutional changes do *not* result in Kondo or intermediate valence behavior in the temperature range of 4-300 K. The Ce moment does not seem to interact strongly with the conduction electrons to form "compensation clouds."

Nevertheless, the *presence* of the Ce moment does appear to be controlled by the nature of the near neighbor transition metal atoms. Upon substitution with Ni, Ce_2Pd_2In evolves into a paramagnet. The data are consistent with a model in which the number and type of near neighbors determine the Ce state. A critical number of near neighbor Ni atoms may cause the Ce f electron to delocalize, resulting in the relatively flat susceptibility curves observed for $x \geq 0.75$.

4. Conclusions

We have investigated the magnetic and electrical properties of the substitution series $Ce_2Ni_{2x}Pd_{2(1-x)}In$. The cerium moment stays roughly constant for $x=0$ to 0.5, with changes mainly in the RKKY interactions. From $x=0.5$ to 1.0, the cerium moment becomes essentially quenched, and the material behaves more like a traditional metal.

Contrary to our initial hopes, throughout this substitution series, Kondo-like or intermediate valence anomalies are not observed, underscoring the delicate nature of such states.

Acknowledgments

This work was supported by the Office of Naval Research. We would like to thank R.A. Gordon for helpful advice. Y. I. would also like to acknowledge financial support from a National Physical Science Consortium fellowship.

TABLE 1

Lattice parameters for $Ce_2Ni_{2x}Pd_{2(1-x)}In$.

x	a (Å)	c (Å)	Volume (Å^3)
0.0	7.805 (1)	3.915 (1)	238.5
0.25	7.751 (2)	3.890 (1)	233.7
0.5	7.682 (2)	3.861 (1)	227.8
0.625	7.649 (2)	3.841 (1)	224.7
0.75	7.608 (3)	3.795 (1)	219.7
1.0	7.526 (1)	3.723 (1)	210.9

TABLE 2

Curie-Weiss fit parameters for $Ce_2Ni_{2x}Pd_{2(1-x)}In$, with x=0 to 0.5 and a fit range of 100 to 320 K.

x	μ_{eff} (μ_B)	θ (K)	χ_o (emu/g)	σ
0.0	2.45 (4)	20 (2)	4 (2) x 10^{-7}	1.4 x 10^{-3}
0.25	2.39 (5)	4 (3)	7 (2) x 10^{-7}	1.5 x 10^{-3}
	2.46 (6)	-39 (5)	8 (3) x 10^{-7}	1.4 x 10^{-3}

List of Figure Captions

Fig. 1. Lattice parameters as a function of x in $Ce_2Ni_{2x}Pd_{2(1-x)}In$. Dashed lines indicate expected values based on x=0.0 to 0.5.

Fig. 2. a) Magnetic susceptibilities and b) inverse susceptibilities for $Ce_2Ni_{2x}Pd_{2(1-x)}In$ upon heating.

Fig. 3. Inverse susceptibility of Ce_2Pd_2In on cooling and heating.

Fig. 4. Scaled electrical resistivity for $Ce_2Ni_{2x}Pd_{2(1-x)}In$ for a) x=0.25 to 1.0 and b) for x=0.0 (Ce_2Pd_2In).

References

1. R.A. Gordon, Y. Ijiri, C.M. Spencer, and F.J. DiSalvo, *J. Alloys Comp.*, in press.

2. F. Fourgeot, B. Chevalier, P. Gravereau, L. Fournès, J. Etourneau, *J. Alloys Comp., 218* (1995), 90.

3. F. Hulliger, *J. Alloys Comp., 217* (1995), 164.

4. A. Purvanto, R.A. Robinson, L. Havela, V. Sechovsky, P. Svoboda, H. Nakotte, K. Prokes, F.R. deBoer, A. Seret, J.M. Winand, J. Rebizant, and J.C. Spirlet, *Phys. Rev. B, 50* (1994), 6792.

5. P. de V. DuPlessis, A.M. Strydom, and A. Baran, *Physica B 206/207* (1995), 495.

6. F. Mirambet, B. Chevalier, L. Fournès, P. Gravereau, and J. Etourneau, *J. Alloys Comp., 203* (1994), 29.

7. L. Havela, V. Sechovsky, P. Svoboda, M. Divis, H. Nakotte, K. Prokes, F.R. deBoer, A. Purwanto, R.A. Robinson, A. Seret, J.M. Winand, J. Rebizant, J.C. Spirlet, M. Richter, and H. Eschrig, *J. Appl. Phys., 76* (1994), 6214.

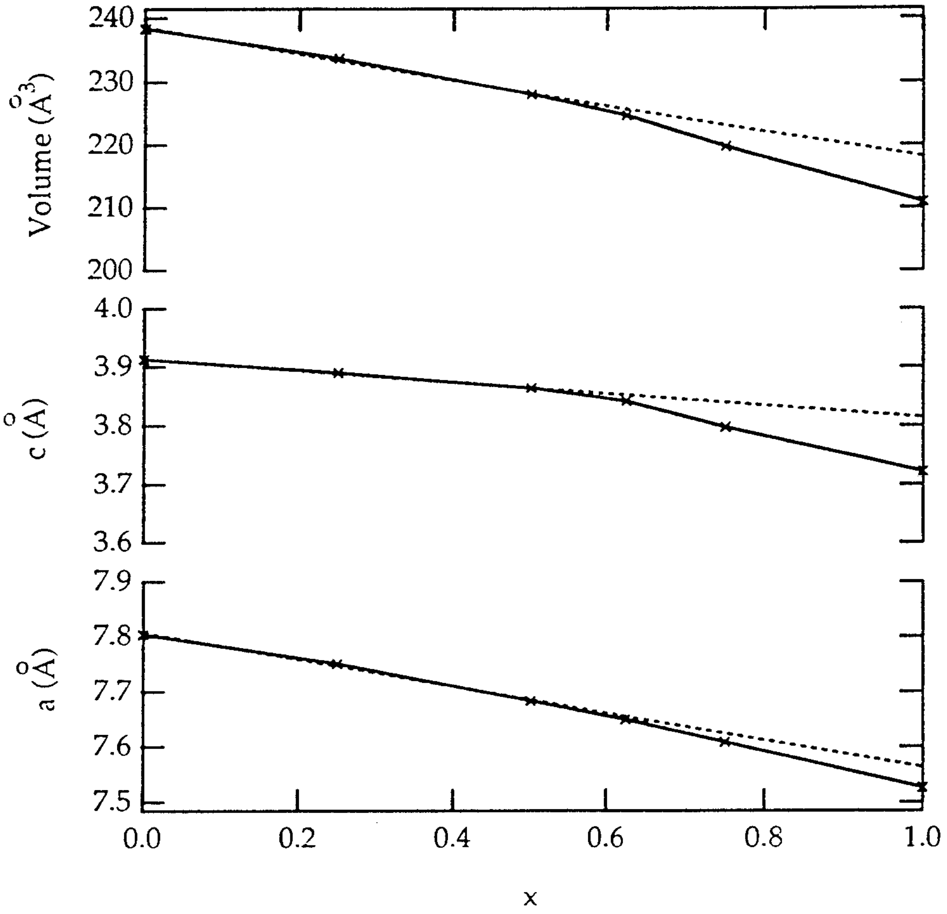
8. P.E. Werner, L. Eriksson, and M. Westdhal, *J. Appl. Crystallogr., 18* (1985), 367.

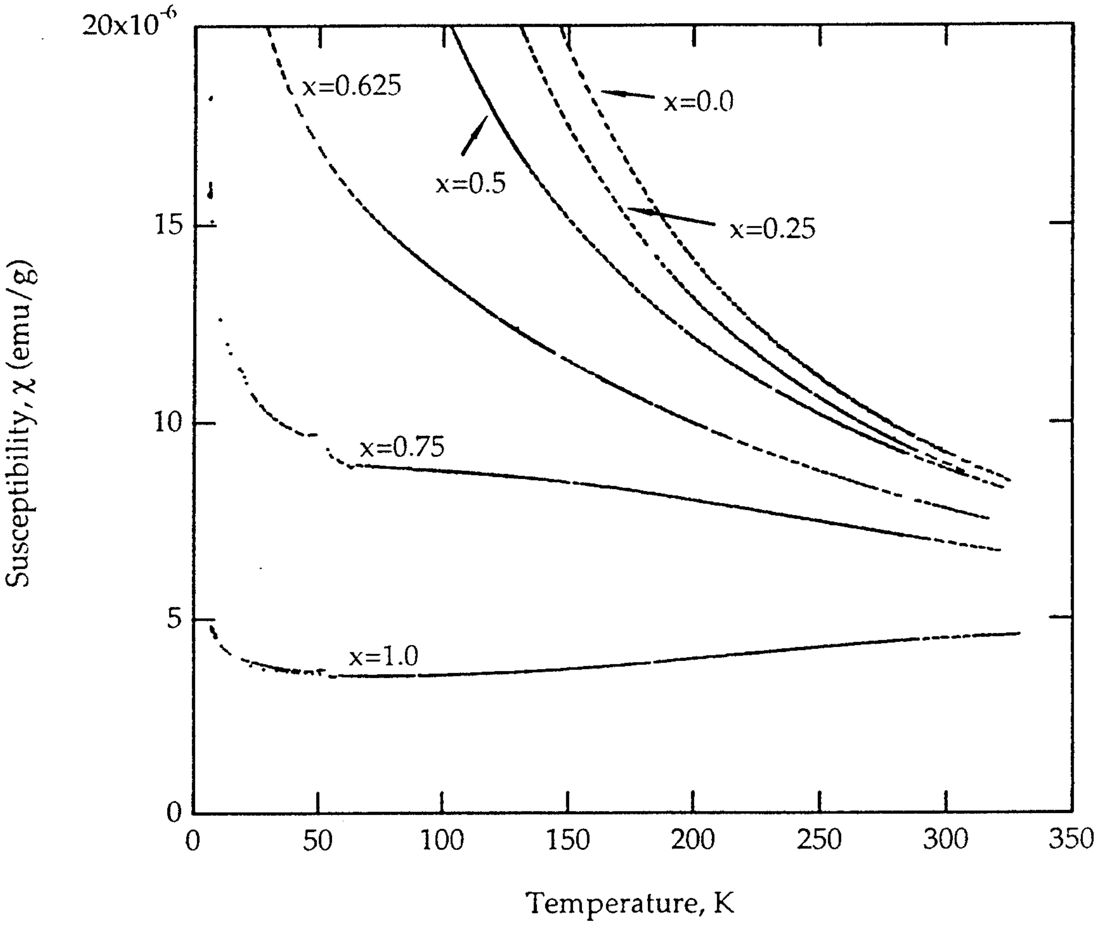
9. D.R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, CRC Press, 1993, Vol. 74, Section 9, 53.

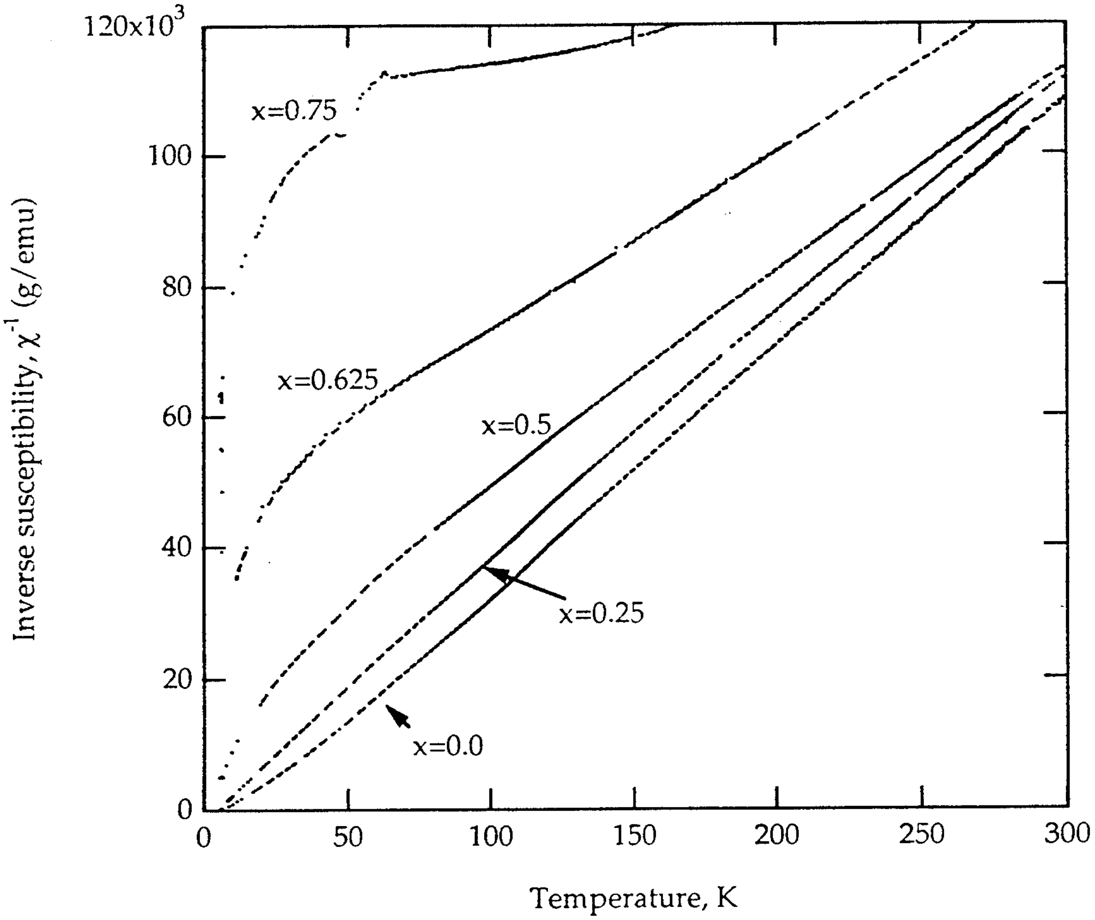
10. D.L. Bish and R.C. Reynolds Jr., in D.L. Bish and J.E. Post (eds.), *Reviews in Mineralogy,* Mineralogical Society of America, 1989, Vol. 20, Chap. 4.

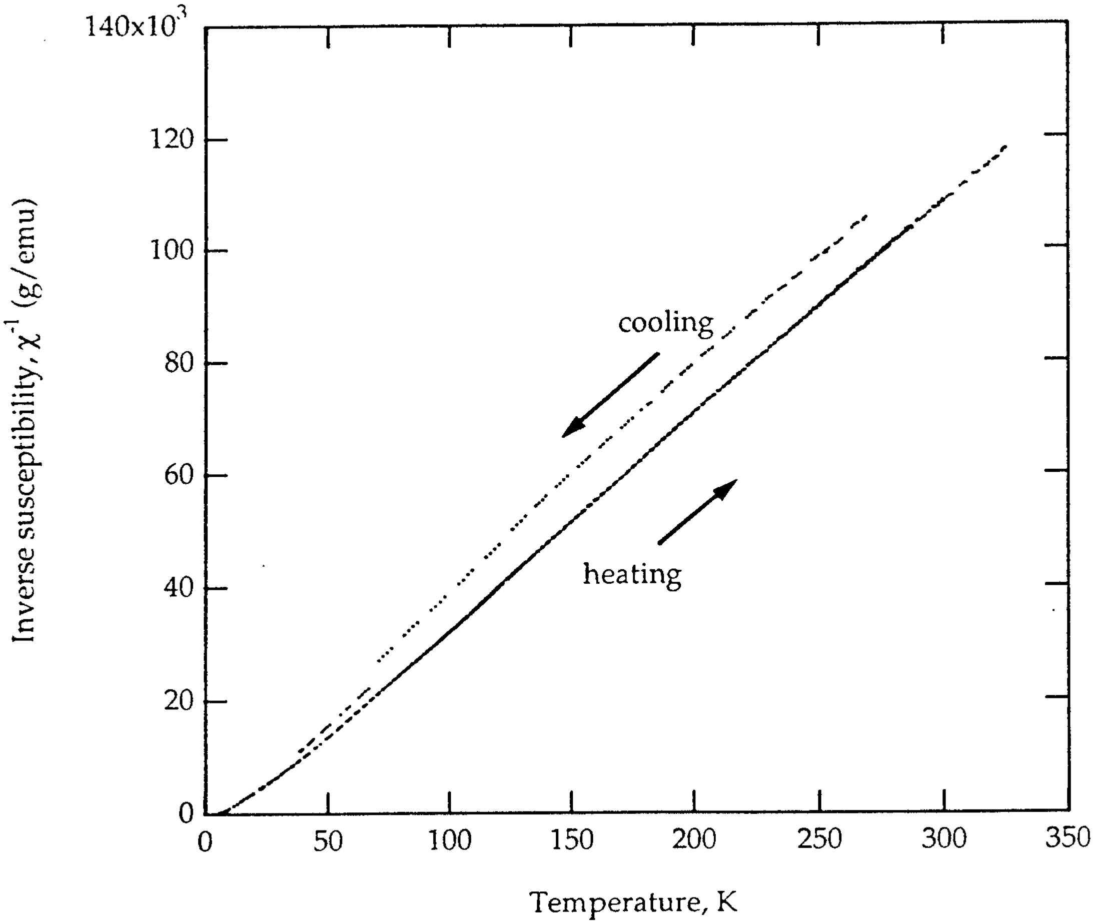
11. V.K. Pecharsky, O.-B. Hyun, and K.A. Gschneider, Jr., *Phys. Rev. B, 47* (1993) 11839.

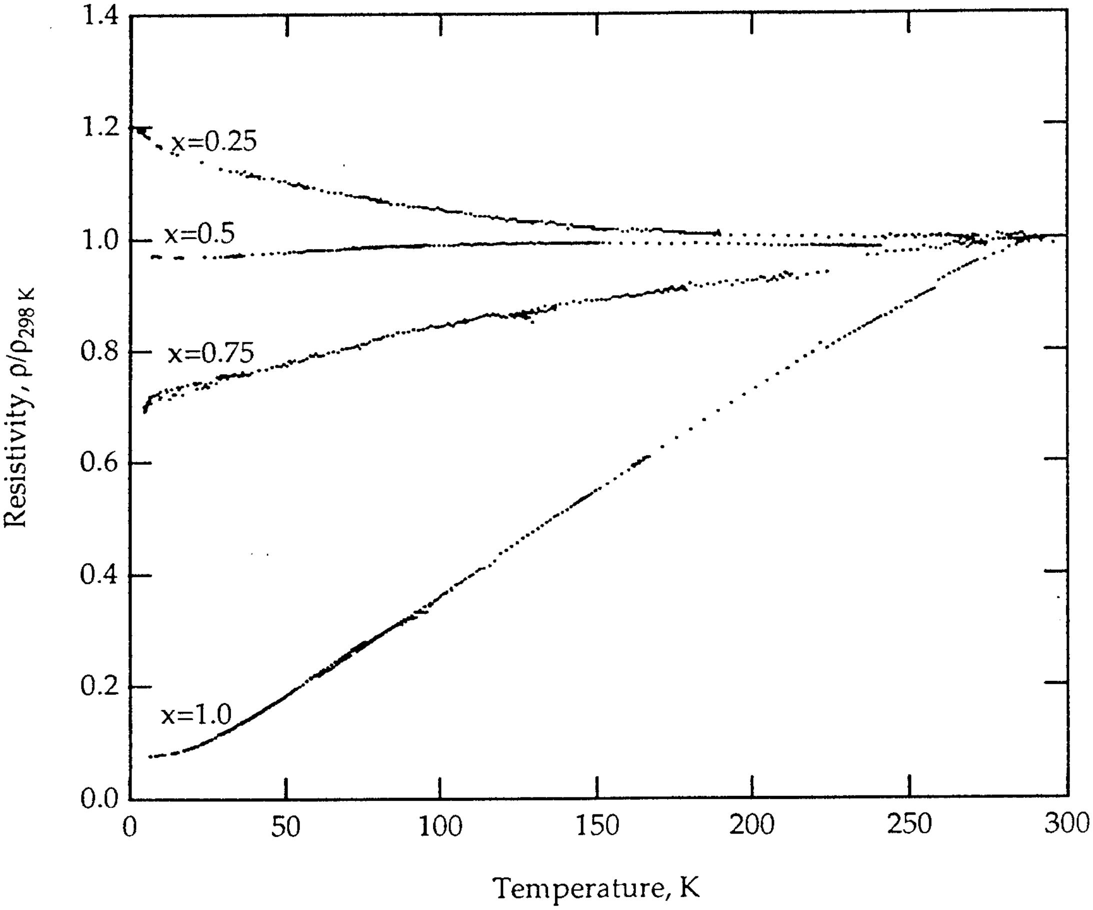
12. P.R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw Hill, 1969.

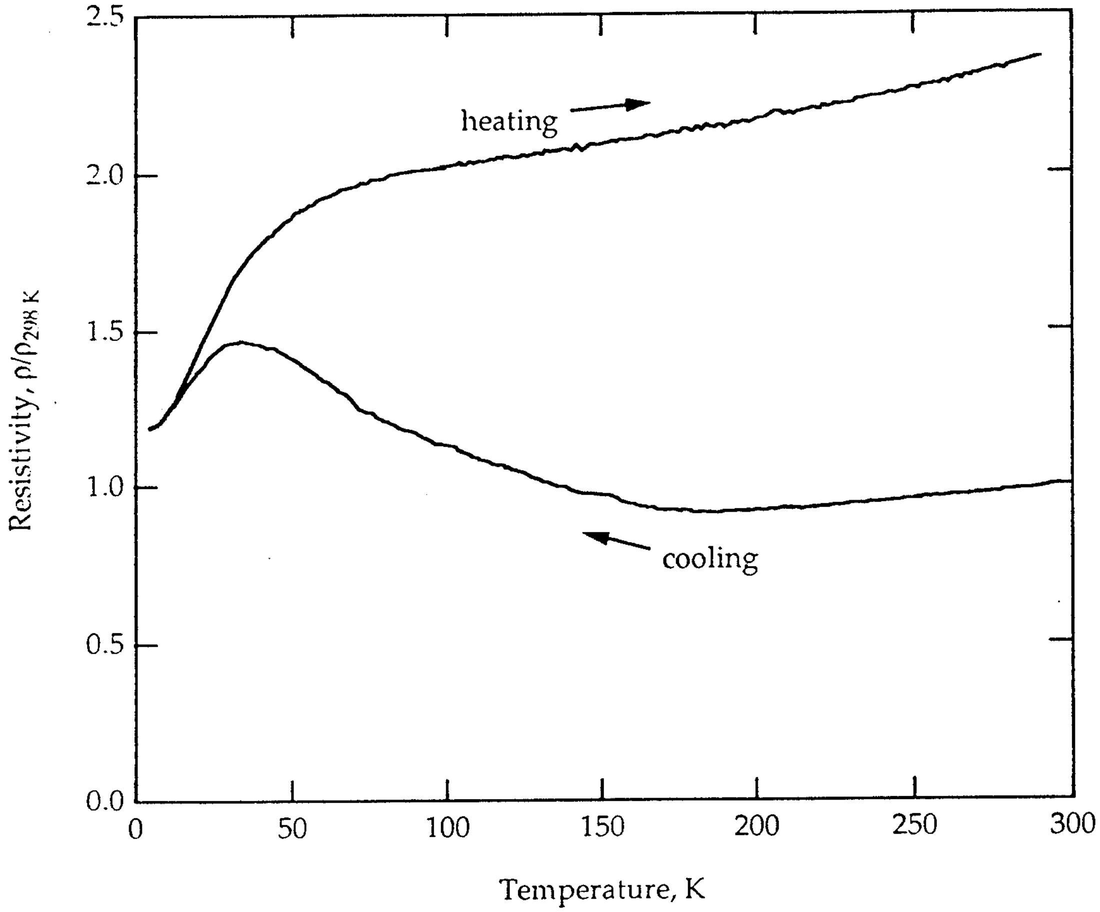

Volume (Å^3)
240
230
220
210
200
c (Å)
4.0
3.9
3.8
3.7
3.6
a (Å)
7.9
7.8
7.7
7.6
7.5
0.0
0.2
0.4
0.6
0.8
1.0
x


20x10^-6
15
10
5
0
Susceptibility, χ (emu/g)
0
50
100
150
200
250
300
350
Temperature, K
x=0.625
x=0.5
x=0.0
x=0.25
x=0.75
x=1.0


120x10^3
100
80
60
40
20
0
0
50
100
150
200
250
300
Inverse susceptibility, χ^{-1} (g/emu)
Temperature, K
x=0.75
x=0.625
x=0.5
x=0.25
x=0.0


140x10^3
120
100
80
60
40
20
0
Inverse susceptibility, χ^{-1} (g/emu)
0
50
100
150
200
250
300
350
Temperature, K
cooling
heating


1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
x=0.25
x=0.5
x=0.75
x=1.0
Resistivity, $\rho/\rho_{298\ K}$
Temperature, K


2.5
2.0
1.5
1.0
0.5
0.0
0
50
100
150
200
250
300
heating
cooling
Resistivity, ρ/ρ298 K
Temperature, K

**************************end page 6******************************

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

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

Dr. John Fischer (1)
Chemistry Division, Code 385
NAWCWD - China Lake
China Lake, CA 93555-6001

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

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

* Number of copies required

**************************end page 7******************************