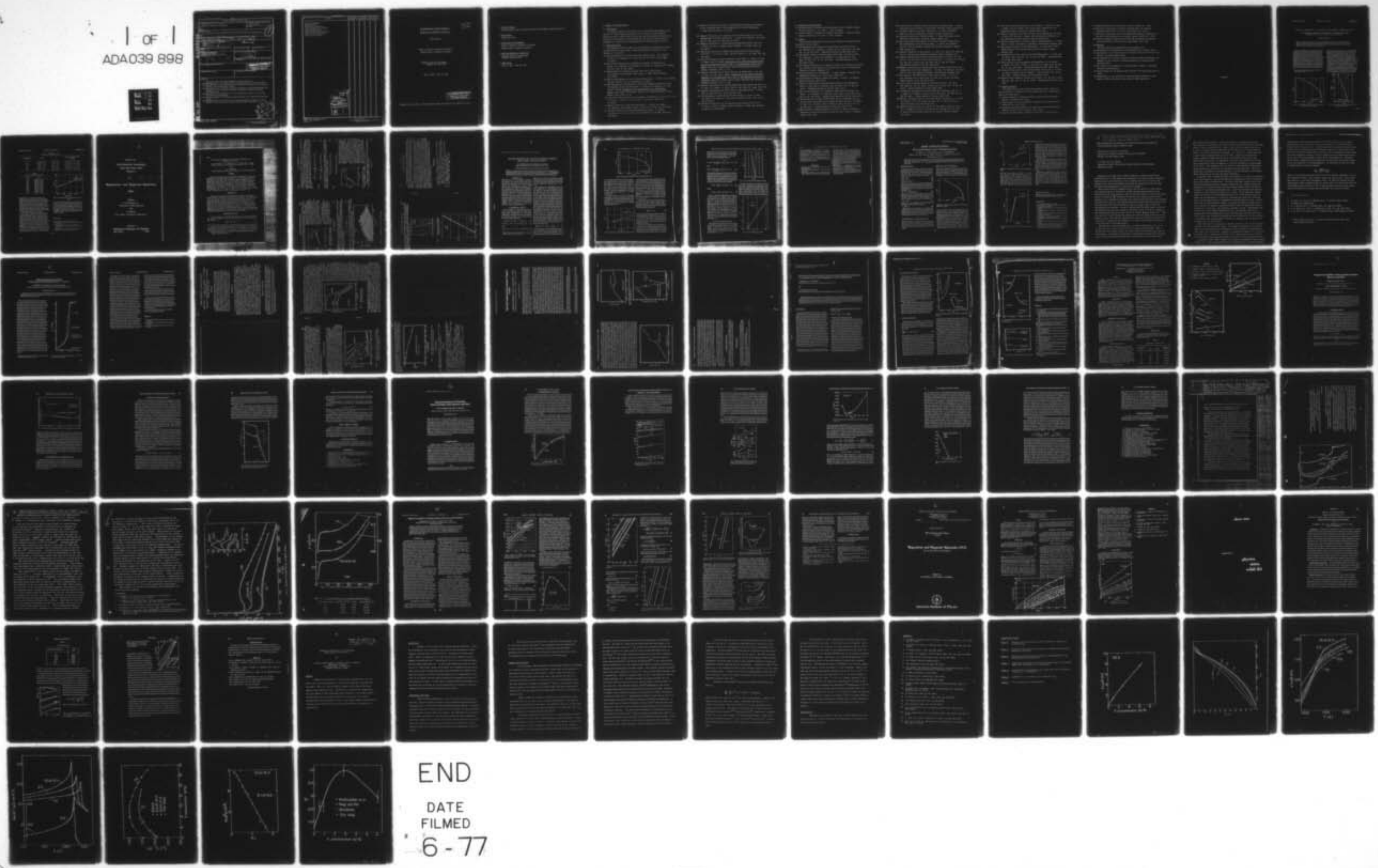
AD-A039 898   CLARKSON COLL OF TECHNOLOGY POTSDAM N Y   F/G 20/3
AN EXPERIMENTAL STUDY OF MAGNETIC MATERIALS AND MAGNETIC TRANSI--ETC(U)
JUN 76 E E ANDERSON, S ARAJS   N00014-76-C-0051

UNCLASSIFIED   NL

1 OF 1
ADA039 898



END
DATE
FILMED
6-77

ADA039898

DDC FILE COPY

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
Clarkson College of Technology

(6)

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

(1)

3. REPORT TITLE
An Experimental Study of Magnetic Materials and Magnetic Transitions.

(9)

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Final Technical Report, 1 Jul 70 - 30 Jun 76,

5. AUTHOR(S) (Last name, first name, initial)
Anderson, Elmer E. /Anderson
(10)
Arajs, Sigurds /Arajs

6. REPORT DATE
(15)

7a. TOTAL NO. OF PAGES

7b. NO. OF REFS

8a. ~~CONTRACT OR GRANT NO~~
N00014-76-C-0051 new
(Formerly N00014-70-A-0311-0001

b. PROJECT NO.

c. (11) 30 Jun 76

d.

9a. ORIGINATOR'S ~~REPORT NUMBER~~(S)
(12) 86p.

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. AVAILABILITY/LIMITATION NOTICES

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

13. ABSTRACT

The most important accomplishments of this project are

the (1) Development of a new method for the determiniation of critical indices;

the (2) Determination of critical indices for Europium, Rutetium and Yttrium Iron Garnets, and nickel-copper alloys,

(3) The emergence of a unified correlation between the Néel temperatures and anomalies in the electrical transport properties of numerous binary chromium alloys,

the (4) New studies of the behavior of localized magnetic moment in itinerant electron antiferromagnetic,

the (5) Partial mapping of the magnetic phase diagram of the gadolinium-samarium system, and the

(6) Demonstration of the existence of localized magnetic moments in paramagnetic nickel and binary nickel alloys at high temperatures,

D D C
MAY 24 1977
C

DD FORM 1 JAN 64 1473

Security Classification

085000

1B

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	
Critical Phenomena						
Magnetization						
Electrical Resistivity						
Samarium-Gadolinium System						
Antiferromagnetism						
Chromium and Chromium Alloys						
Nickel and Nickel Alloys						
Iron and Iron Alloys						

White Section ☑
Buff Section ☐
UNANNOUNCED ☐
JUSTIFICATION Per Form 50 on file
DISTRIBUTION/AVAILABILITY CODES

Dist.	AVAIL. and/or SPECIAL	
A		

318-004
(2) JAO

An Experimental Study of Magnetic Materials and Magnetic Transitions

Final Report

Elmer E. Anderson, Professor of Physics
Sigurds Arajs, Professor of Physics

Clarkson College of Technology
Potsdam, New York 13676

July 1, 1970 - June 30, 1976

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

Prepared for the Office of Naval Research under the contract No. N00014-76-C-0051

1. Title of Project

   An Experimental Study of Magnetic Materials and Magnetic Phase Transition

2. Grant Number

   N00014-76-C-0051

3. Co-Principal Investigators

   Elmer E. Anderson, Professor of Physics

   Sigurds Arajs, Professor of Physics

4. Name and Address of Institution

   Clarkson College of Technology
   Potsdam, New York 13676

5. Time Period

   July 1, 1970 - June 30, 1976

6. Summary of Accomplishments

6.1 Introduction

The primary purpose of the project was to investigate experimentally the behavior of various magnetic materials in the vicinity of their magnetic transitions and to compare these results with existing theoretical predictions. During the later stages of the investigations the scope of the project was broadened to include also the manifestations of localized magnetic moments.

6.2 Published Papers

The following scientific papers have been published resulting from studies associated with the above grant. These publications are attached to this document as in Appendix.

(1) Critical Exponent β for Nickel and Nickel-Copper Alloys. E.E. Anderson, S. Arajs, A.A. Stelmach, B.L. Tehan, and Y.D. Yao, Phys. Letters 36A, 173 (1971).

(2) The Critical Exponents for the Magnetic Properties of Europium Iron Garnet. A.A. Stelmach, E.E. Anderson, B.L. Tehan, S. Arajs, and J.P. Rameika, AIP Conf. Proc. 5, 1240 (1972).

(3) Magnetization of Lutetium Iron Garnet Near the Critical Point. A.A. Stelmach, E.E. Anderson, and S. Arajs, J. Phys. Chem. Solids 34, 1343 (1973).

(4) The Critical Exponent of an δ of Yttrium Iron Garnet. S. Arajs, A.A. Stelmach, and E.E. Anderson, Int. J. Magnetism 4, 173 (1973).

(5) Néel Temperatures and Anomalies in Electrical Transport Properties of Antiferromagnetic Binary Chromium Alloys. S. Arajs, E.E. Anderson, K.V. Rao, and H.U. Åström, Proceeding of the International Conf. of Magnetism ICM-73, 22-28 August 1973, Moscow, USSR, Vol. VI (Publishing House "Nauka", Moscow, USSR, 1976), p. 150.

(6) First Order Phase Transition in the Magnetic Susceptibility of Cr-1.37 at.% Si. L. Hedman, K. Svensson, K.V. Rao, and S. Arajs, Phys. Letters 45A, 175 (1973).

(7) Magnetic Properties of Gd-Rich Gd-Sm Alloys. S. Arajs, D.L. Adour, E.E. Anderson, T.F. DeYoung, and K.V. Rao, AIP Conf. Proc. 18, 362 (1974).

(8) Spin-Flip Transition in the Chromium-Tungsten System. L. Hedman, K. Svensson, K.V. Rao, S. Arajs, and H.U. Åström, J. Low Temp. Phys. 14, 545 (1974).

(9) Magnetic Susceptibility Studies of Polycrystalline Chromium and Chromium-0.3 at.% Tungsten Alloy in the Neighborhood of the Néel Temperature, J. Magn. Mag. Materials 1, 141 (1975).

(10) Magnetic Properties of Cr Containing Dilute Concentrations of Co in the Neighborhood of the Néel Temperature. S. Arajs, E.E. Anderson, J.R. Kelly, and K.V. Rao, AIP Conf. Proc. 24, 412 (1975).

(11) Magnetic Susceptibility of Polycrystalline Samarium Between 4 and 300 K. S. Arajs, K.V. Rao, L. Hedman, and H.U. Åström, J. Low Temp. Phys. 21, 134 (1975).

(12) Electrical Resistivity of Nickel-Rich Nickel-Chromium Alloys Between 4 and 300 K. Y.D. Yao, S. Arajs, and E.E. Anderson, J. Low Temp. Phys. 21, 369 (1975).

(13) First-Order Magnetic Phase Transition in Cr-Si Alloys. S. Arajs, K.V. Rao, L. Hedman, and H.U. Åström, Proceedings of the 14th International Conference on Low Temperature Physics, Vol. 3 - Low Temperature Properties of Solids, edited by M. Krusius and M. Vuorio (North-Holland Publishing Company, Amsterdam, 1975). p. 231.

(14) Magnetic Susceptibility of Pd-Ce Alloys at Low Temperatures. K.V. Rao, S. Arajs, Y.D. Yao, and L. Hedman, Proceedings of the 14th International Conference on Low Temperature Phys., Vol. 3 - Low Temperature Properties of Solids, edited by M. Krusius and M. Vuorio (North-Holland Publishing Company, Amsterdam, 1975), p. 398.

(15) Magnetic Susceptibility of Chromium-Rutheuism Alloys Between 300 and 600 K. S. Arajs, C.A. Moyer, J.R. Kelly, and K.V. Rao, Phys. Rev. B 12, 2747 (1975).

(16) Magnetic Susceptibility of Ni-Al Alloys at High Temperatures. S. Arajs and J.R. Kelly, AIP Conf. Proc. 29, 284 (1976).

(17) Antiferromagnetic Susceptibility of Cr-Re Alloys. S. Arajs, G. Kote, C.A. Moyer, J.R. Kelly, K.V. Rao, and E.E. Anderson, phys. stat. sol. (b) 74, K23 (1976).

(18) Electrical Resistivity of Iron-Vanadium Alloys Between 78 and 1200 K. W. Teoh, S. Arajs, D. Abukay, and E.E. Anderson, J. Magn. Mag. Materials (accepted for publication).

6.2 Reports Not Included Above

(1) The Magnetization of Nickel and Nickel-Copper Alloys. Clarkson College Technical Report No. 1-71, Sept. 1, 1971, 39 pages.

(2) Critical Magnetic Properties of Europium Iron Garnet. Clarkson College Technical Report No. 2-71, Nov. 1, 1971, 30 pages.

6.3 Tables

The following tables have been given the principal investigators based on studies of this project:

(1) The Magnetization of Lutetium Iron Garnet Near the Critical Point. E.E. Anderson, A.A. Stelmach, S. Arajs, and B.L. Tehan, Bull. Am. Phys. Soc. II, 15, 825 (1970). (Winnipeg Meeting of the APS June 1970).

(2) The Magnetic Behavior of Nickel-Copper Alloys Near the Critical Point. E.E. Anderson, S. Arajs, A.A. Stelmach, B.L. Tehan, and Y.D. Yao, Bull. Am. Phys. Soc. II, 16, 394 (1971). (Cleveland Meeting of the APS, March 1971).

(3) The Critical Exponents for the Magnetic Properties of Europium Iron Garnet. A.A. Stelmach, E.E. Anderson, B.L. Tehan, and S. Arajs, 17th Magnetism Conference, Chicago, November 1971.

(4) Critical Phenomena in Ferromagnets. S. Arajs, Seminar, Laboratory for Fundamental Research, U.S. Steel Corp., March 1971.

(5) Manifestations of Magnetic Moments in Solids. S. Arajs, Colloquium, McGill University, April 1971.

(6) Magnetic Susceptibility of Iron-Aluminum Alloys in the Paramagnetic State, S. Arajs and E.E. Anderson, Bull. Am. Phys. Soc. II, 16, 584 (1971). (Washington Meeting of the APS, April 1971).

(7) The Critical Exponents for the Magnetic Properties of Lutetium Iron Garnet. A.A. Stelmach, E.E. Anderson, and S. Arajs, Bull. Amer. Phys. Soc. II, 17, 300 (1972). (Atlantic City Meeting of the APS, March 1972).

(8) Applications of the Kouvel-Fisher Method for the Determination of the Critical Points from Electrical Transport Property Data, A.A. Stelmach, S. Arajs, C.D. Levermore, and E.E. Anderson, Bull. Am. Phys. Soc. II, 18, 359 (1973). (San Diego Meeting of the APS, March 1973).

(9) Manifestations of Magnetic Moments in Solids. S. Arajs, Colloquium, Department of Solid State Physics, Royal Institute of Tech., Stockholm, Sweden, August 1973.

(10) Static Aspects of Magnetic Phase Transitions and Scaling Laws. S. Arajs, Colloquium, Royal Institute of Technology, Stockholm, Sweden, August 1973.

(11) Transport Properties and Phase Transitions. S. Arajs, Colloquium, Royal Institute of Technology, Stockholm, Sweden, August 1973.

(12) Transport Properties of Chromium Alloys. S. Arajs, Colloquium, Royal Institute of Technology, Stockholm, Sweden, August 1973.

(13) Néel Temperatures and Anomalies in Electrical Transport Properties of Antiferromagnetic Binary Chromium Alloys. S. Arajs, E.E. Anderson, K.V. Rao, and H.U. Åström, International Magnetism Conference, Moscow, USSR, August 1973.

(14) Magnetic Properties of Gd-Sm Alloys. S. Arajs, D.L. Adour, E.E. Anderson, and T.F. DeYoung, 19th Magnetism Conference, Boston, December 1973.

(15) Magnetic Susceptibility Studies of Polycrystalline Cr and Cr-3 at .% W Alloy in the Neighborhood of the Néel Temperature. L. Hedman, H.U. Åström, K.V. Rao, and S. Arajs, Bull. Am. Phys. Soc. II, 19, 230 (1974). (Philadelphia Meeting of the APS, March 1974).

(16) Magnetic Properties of Cr Containing Dilute Concentrations of Co in the Neighborhood of the Néel Temperature. S. Arajs, E.E. Anderson, J.R. Kelly, and K.V. Rao, 20th Magnetic Conference, San Francisco, December 1974.

(17) The Deviation from Matthiessen's Rule of Ni-Cr Alloys. Y.D. Yao, E.E. Anderson, and S. Arajs, Bull. Am. Phys. Soc. II, 20, 347 (1975). (Denver Meeting of the APS, March 1975).

(18) Does Ce Have a Magnetic Moment in Dilute Pd-Ce Alloys? K.V. Rao, E.E. Anderson, Y.D. Yao, and S. Arajs, Bull. Am. Phys. Soc. II, 20, 320 (1975). (Denver Meeting of the APS, March 1975).

(19) The Magnetic Susceptibility of Polycrystalline Sm Between ψ and 300 K. L. Hedman, H.U. Åström, S. Arajs, and K.V. Rao, Bull. Am. Phys. Soc. II, 20, 345 (1975). (Denver Meeting of the APS, March 1975).

(20) Magnetic Susceptibility of Cr-Rv Alloys Between 300 and 600 K. S. Arajs, J.R. Kelly, and K.V. Rao, Bull. Am. Phys. Soc. II, 20, 459 (1975). (Denver Meeting of the APS, March 1975).

(21) Magnetic Susceptibility of Cr and Cr-Si Alloys with 0.46 and 3.19 at .% Si. L. Hedman, A. Kjerulf, K. Svensson, H.U. Åström, K.V. Rao, and S. Arajs, Swedish National Committee for Physics, Göteborg, Sweden, June 1975).

(22) First-Order Magnetic Transition in Cr-Ci Alloys. S. Arajs, K.V. Rao, L. Hedman, and H.U. Åström, 14th International Conference on Low Temperature Physics, Ontaniemi, Finland, August 1975.

(23) Magnetic Susceptibility of Pd-Ce Alloys at Low Temperatures, K.V. Rao, S. Arajs, Y.D. Yao, and L. Hedman, 14th International Conference on Low Temperature Physics, Otaniemi, Finland, August 1975.

(24) Magnetic Susceptibility of Ni-Al Alloys at High Temperatures. S. Arajs and J. R. Kelly, 21st Magnetic Conference, Philadelphia, December 1975.

(25) Dilutization Treatment of the Kondo Effect. Y.D. Yao and S. Arajs, Annual Meeting of the Chinese Physical Society, Tamsui, Taiwan, February 1976.

(26) Paramagnetism in Ni-Ta Alloys at Elevated Temperatures. S. Arajs and J.R. Kelly, Bull. Am. Phys. Soc. II, 21, 442 (1976). (Atlanta Meeting of the APS, March 1976).

(27) Electrical Resistivity and Magnetic Susceptibility of Cr-Re Alloys, D. Abukay, K.V. Rao, S. Arajs, G. Kote, and C.A. Moyer, Bull. Am. Phys. Soc. II, 21, 442 (1976). (Atlanta Meeting of the APS, March 1976).

(28) Electrical Resistivity of Fe-V Alloys Between 78 and 1200 K. W. Teoh, S. Arajs, D. Abukay, and E.E. Anderson. Bull. Am. Phys. Soc. II, 21, 442 (1976). (Atlanta Meeting of the APS, March 1976).

(29) Magnetic Phase Diagram of Cr-Rich Cr-Si Alloys. K.V. Rao and S. Arajs, Bull. Am. Phys. Soc. II, 21, 821 (1976). (Quebec Meeting of APS, June 1976).

6.5 Graduate Students

The studies done on this project have produced 3 Ph.D. and 5 M.S. theses in physics. Recipients of these degrees and their corresponding theses are listed below:

(1) Critical Behavior of Europium, Lutetium, and Yttrium Iron Garnets, Alfred A. Stelmach, Ph.D., 1972.

(2) Contributions to Localized Moments in Transition Rare Earth Alloys, Yeong Der Yao, Ph.D., 1974.

(3) Electrical Transport Properties of Itinerant and Localized Electron Magnetic Systems, Tice F. DeYoung, Ph.D., 1976.

(4) Yeon Der Yao received M.S. degree in 1971 without written thesis.

(5) Magnetic Properties of Gd-Sm Alloys, David L. Adour, M.S., 1975.

(6) Electrical Resistivity of Chromium, Chromium-Gold, and Chromium-Palladium Alloys from 77 to 700 K, Aslan Eroglu, M.S., 1975.

(7) Electrical Resistivity and the Ferromagnetic-Paramagnetic Transition of Ni, Ni-Si Solid Solutions Fe, and Fe_3Si, James J. Karol, M.S., 1975.

(8) Effects of Magnetic Transitions and Critical Fluctuations on the Electrical Resistivity of Cr-Re Alloys, Dogan Abukay, M.S., 1975.

6.6 Abstract

The most important accomplishments of this project are

(1) Development of a new method for the determination of critical indices

(2) Determination of critical indices for Europium, Rutetium and Yttrium Iron Garnets, and nickel-copper alloys

(3) The emergence of a unified correlation between the Néel temperatures and anomalies in the electrical transport properties of numerous binary chromium alloys

(4) New studies of the behavior of localized magnetic moment in itinerant electron antiferromagnetic

(5) Partial mapping of the magnetic phase diagram of the gadolinium-samarium system

(6) Demonstration of the existence of localized magnetic moments in paramagnetic nickel and binary nickel alloys at high temperatures

APPENDIX

CRITICAL EXPONENT β FOR NICKEL AND NICKEL-COPPER ALLOYS *

E. E. ANDERSON, S. ARAJS, A. A. STELMACH, B. L. TEHAN and Y. D. YAO
Clarkson College of Technology, Potsdam, New York 13676, USA

Received 20 July 1971

A linear extrapolation of the plot of the square of the applied magnetic field versus break-point temperature is shown to lead to an erroneous Curie temperature, which, in turn, can result in two values of the critical exponent β. Careful determinations of Curie temperatures result in a value for β of about 0.34 for nickel and nickel-copper alloys.

Some of the difficulties associated with using the kink-point method for studying the spontaneous magnetization near the Curie temperature have been discussed recently by Arrott [1]. He suggests that one possible source of error in the value of the exponent β is in the determination of the break-point temperatures, T_t, because the breadth of the transition increases as larger applied fields are used. However, this objection is not serious because the breaks are quite sharp for the low-field points which determine the behavior of the magnetization in the important temperature regime close to T_c. A second possible source of error cited by Arrott is in the determination of the Curie point itself, since some form of extrapolation to zero field must be employed. Wojtowicz and Rayl, using molecular field theory, showed that in low applied fields the break-point temperature should vary linearly with the square of the applied field [2]. Hence, it has been our practice to determine T_c by an extrapolation of the best straight line through a plot of H_a^2 versus T_t. However, in our recent studies of the magnetization of nickel-copper alloys [3] we found that these plots were not linear and, furthermore, that adherence to a straight line would result in a value of T_c that would be

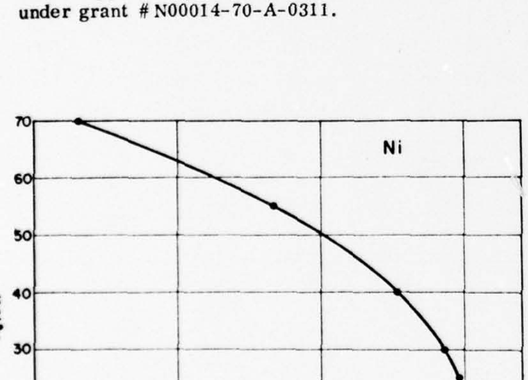


Fig. 1. Applied magnetic field (H_a) versus break-point temperature (T_t) for nickel.

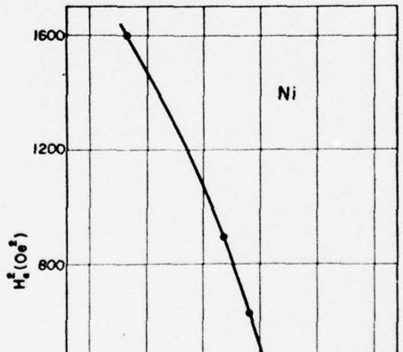


Fig. 2. Square of the applied field versus break point temperature for nickel.

---

* Work supported by the Office of Naval Research under grant # N00014-70-A-0311.

Table 2
Results for nickel-copper system

Cu Concentration (At %)	T_c(°K)	β	Observed range of validity $\epsilon = \frac{T_c - T}{T_c}$
0	626.055 ± 0.005	0.346 ± 0.007	$2.4 \times 10^{-5} < \epsilon < 5.6 \times 10^{-3}$
4.64	575.60 ± 0.01	0.34 ± 0.01	$3.0 \times 10^{-5} < \epsilon < 4.7 \times 10^{-3}$
9.31	525.95 ± 0.01	0.34 ± 0.01	$6.0 \times 10^{-5} < \epsilon < 2.6 \times 10^{-3}$
14.0	475.39 ± 0.04	0.33 ± 0.01	$3.8 \times 10^{-4} < \epsilon < 6.1 \times 10^{-3}$
18.8	424.9 ± 0.3	0.33 ± 0.01	$1.9 \times 10^{-2} < \epsilon < 9.2 \times 10^{-2}$

Table 1
Low-field break points for nickel

H_a(Oe)	T_t(°K)
3.4	626.053 ± 0.005
10.6	626.045 ± 0.005
14.6	626.040 ± 0.005
17.4	626.028 ± 0.005
21.2	626.011 ± 0.005
25.0	625.981 ± 0.005
29.9	625.936 ± 0.005
40.0	625.764 ± 0.007
55.0	625.333 ± 0.010
70.0	624.653 ± 0.050
95.3	622.545 ± 0.100

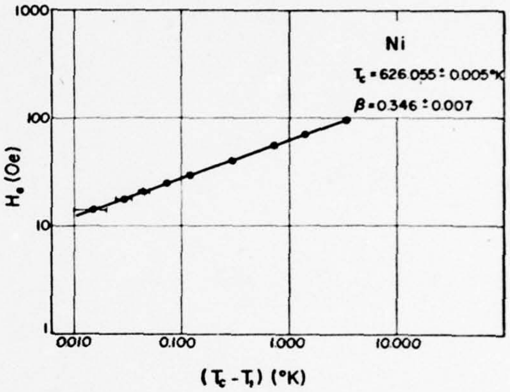


Fig. 3. Determination of the critical exponent β for nickel.

too high. Thus, Arrott's criticism of the Wojtowicz-Rayl extrapolation method appears to be valid (see fig. 2 of ref. [1]). To avoid this pitfall, we obtained T_c for each of the nickel-copper alloys by a consistent extrapolation (to zero field) of plots of H_a, H_a^2 and H_a^3 versus T_t For each alloy measured, the value of T_c obtained in this manner resulted in a single value for the critical exponent β of about 0.34 throughout the temperature range considered.

The results for the nickel-copper alloys raised a question about our recent value for β for pure nickel [4], which was based upon the linear extrapolation method of Wojtowicz and Rayl. Accordingly, we have carefully remeasured sphere A of ref. [4] in very low fields (see table 1). The value of T_c was determined by plotting both H_a and H_a^2 versus T_t and extrapolating to zero field, as shown in figs. 1 and 2. Although there is still some uncertainty in T_c, the value of 626.055°K obtained from these plots is much more reliable than one obtained from a linear extrapolation. Moreover, the new value of T_c yields a single value for β for nickel, as in the case of the nickel-copper alloys (see fig. 3). The experimental results are summarized in table 2. It should be emphasized that while absolute temperatures are valid to only ± 1°K, our relative temperature readings are good to ± 0.005°K. Thus, temperature differences are valid to ± 0.01°K.

References

[1] A. Arrott, J. Appl. Phys. 42 (1971) 1282.
[2] P. J. Wojtowicz and M. Rayl, Phys. Rev. Letters 20 (1968) 1489.
[3] E. E. Anderson, S. Arajs, A. A. Stelmach, B. L. Tehan and Y. D. Yao, Bull. Amer. Phys. Soc. 11, 16 (1971) 394.
[4] S. Arajs, B. L. Tehan, E. E. Anderson and A. A. Stelmach, Phys. Stat. Sol. 41 (1970) 639.

* * * * *

2

Reprint from

AIP Conference Proceedings

Series Editor: Hugh C. Wolfe

Number 5

Magnetism and Magnetic Materials

1971

Editors

C. D. Graham, Jr.

University of Pennsylvania

and

J. J. Rhyne

U.S. Naval Ordnance Laboratory

American Institute of Physics
New York 1972

THE CRITICAL EXPONENTS FOR THE MAGNETIC PROPERTIES OF EUROPIUM IRON GARNET

A. A. Stelmach, E. E. Anderson, B. L. Tehan, and S. Arajs
*Clarkson College of Technology,** Potsdam, New York 13676

and

J. P. Remeika
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

ABSTRACT

The critical exponents for europium iron garnet have been determined from a single crystal grown by the flux method. Magnetic measurements were made with a vibrating sample magnetometer on a spherical specimen about 1/8 inch in diameter. A Néel temperature of 562.380 ± 0.005 °K was obtained by plotting applied magnetic field versus break-point temperature. This value was confirmed by application of the Kouvel-Fisher method in the temperature region directly above and below T_c. The experimental values of the critical exponents are: $\beta = 0.391 \pm 0.001$, $\gamma = 1.32 \pm 0.01$, and $\delta = 4.40 \pm 0.04$. These values satisfy the scaling law, $\beta(\delta-1) = \gamma$.

INTRODUCTION

A study of the magnetic properties of europium iron garnet (EuIG) has been carried out in the critical regime. The sample used in this study was a single crystal grown by the flux method. Magnetic measurements were made using the kink-point method for a spherical specimen of approximately 1/8 inch in diameter in conjunction with a vibrating sample magnetometer, as described elsewhere.[1,2] The critical exponents β, δ, and γ were determined and compared with the scaling prediction, $\beta(\delta-1) = \gamma$. A test of the validity of the value for the Néel temperature, obtained by plotting applied magnetic field as a function of break-point temperature, has been made by application of the Kouvel-Fisher method.

EXPERIMENTAL RESULTS

In the vicinity of the Néel temperature, T_c, a direct study of the critical exponent β has been made for EuIG by use of the defining equation

$$\sigma(T) \sim \epsilon^{\beta}, \text{ for } \epsilon > 0 \tag{1}$$

where $\sigma(T)$ is the zero-field mass magnetization, and $\epsilon = (T_c-T)/T$.

In the case of EuIG, the break-point temperatures obtained from the magnetization-temperature plots were for values of the applied field between 0.9-74.2 Oe. For applied fields larger than 74.2 Oe,

---

* Work supported by the Office of Naval Research under grant number N00014-70-A-0311.

accurate values of break-point temperatures were not possible due to the large uncertainty in choosing the break-point itself. A plot of Ha vs T_t was made in order to determine T_c. By extrapolation of this curve to the zero applied field axis, a value corresponding to T_c = (562.380 ± 0.005)°K was obtained. A log-log plot of Ha vs (T_c-T_t) was linear in the range of $5.34 \times 10^{-5} < \epsilon < 1.28 \times 10^{-2}$ with a corresponding least-square fitted value of $\beta = 0.391 \pm 0.001$ (Fig. 1).

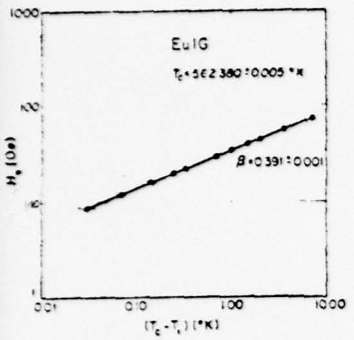


Fig. 1 Determination of the Critical Exponent β for EuIG

The critical exponent δ, which is associated with the variation of the internal magnetic field, H_i, with magnetization at the critical isotherm, is given in terms of the power law expression

$$H_i \sim \sigma(H_i, T_c)^{\delta} . \qquad (2)$$

A log-log plot of H_i vs $\sigma(H_i, T_c)$ for EuIG resulted in a least square value of 4.40 ± 0.04 for the critical exponent δ.

Above T_c, the behavior of the initial mass magnetic susceptibility, χ_o, is described in terms of the critical exponent γ, through the functional relationship

$$\chi_o^{-1} \sim -\epsilon^{\gamma}, \text{ for } \epsilon < 0 . \qquad (3)$$

For EuIG, a plot of σ^2 vs H_i/σ was made in order to determine values of χ_o. As shown in Fig. 2, corresponding values of χ_o^{-1} were obtained by extrapolation of the isotherms to the $\sigma^2 = 0$ axis.

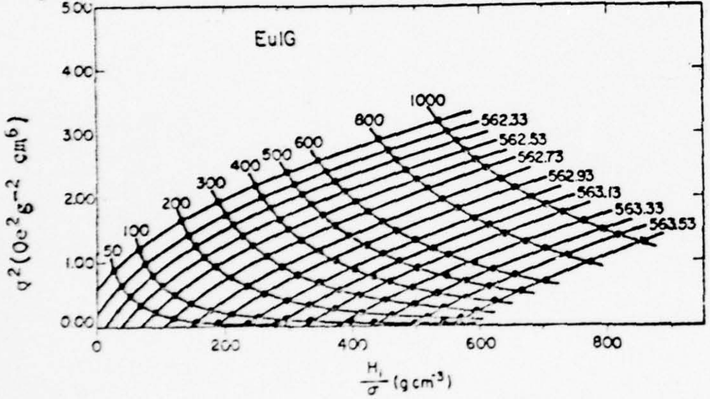


Fig. 2 Isotherms of σ^2 vs H_i/σ for EuIG

A log-log plot of χ_o^{-1} vs (T-T_c) showed Eq. (3) to be valid with a least-square value of $\gamma = 1.32 \pm 0.01$ (see Fig. 3).

In order to confirm the behavior of EuIG in the critical region, use was made of a technique developed by Kouvel and Fisher. This method involves the determination of the quantities $T^+(T_t)$ an $T^*(T)$, which are defined in accordance to whether one is consideri the temperature region directly above or below the critical point. That is,

$$T^+(T_t) \equiv [H_a \frac{d}{dT_t} (H_a^{-1})]^{-1}, \text{ for } T<T_c \qquad (4)$$

while

$$T^*(T) \equiv [\chi_o \frac{d}{dt} (\chi_o^{-1})]^{-1}, \text{ for } T>T_c . \qquad (5)$$

For the limiting cases of T_t and T approaching T_c (from below and above, respectively) these expressions reduce to a functional form which is linear in temperature, namely

$$T^+(T_t) = \frac{1}{\beta} (T_c - T_t), \text{ for } T<T_c \qquad (6)$$

and

$$T^*(T) = \frac{1}{\gamma} (T - T_c), \text{ for } T>T_c . \qquad (7)$$

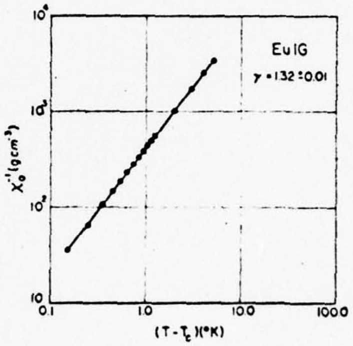


Fig. 3 Determination of the Critical Exponent γ for EuIG

Here the validity of Eqs. (1) and (3) is assumed to give an accurate description of those magnetic properties (i.e., magnetization and susceptibility) in the region of the critical temperature.

A computer program was written for the determination of $T^+(T_t)$ a $T^*(T)$ from plots of H_a^{-1} vs T_t an χ_o^{-1} vs T. From the plots of $T^+($ vs T_t and $T^*(T)$ vs T (Figs. 4 and a value of T_c = (562.38)°K was obtained by extrapolation of the resulting straightline curves to the zero $T^+(T_t)$ and $T^*(T)$ axes. The value of T_c is in good agreement with the result obtained from the plot of H_a vs T_t.

According to scaling theory,[4-6] the three critical exponents β δ, and γ should satisfy the relationship.

$$\beta(\delta - 1) = \gamma . \qquad (8)$$

sing our experimentally determined values of β and δ, this equa-ion implies a value of $\gamma = 1.33 \pm 0.02$. Thus, in the case of uIG, the scaling law is seen to be valid for our experimental lue of $\gamma = 1.32 \pm 0.01$ (see Fig. 3).

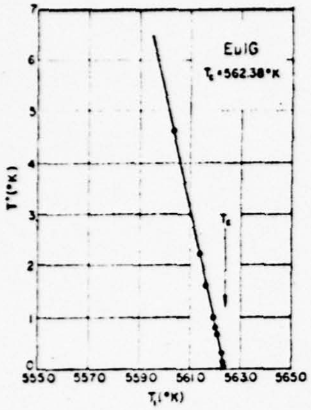


Fig. 4 $T^+(T_t)$ Versus Break-Point Temperature for EuIG

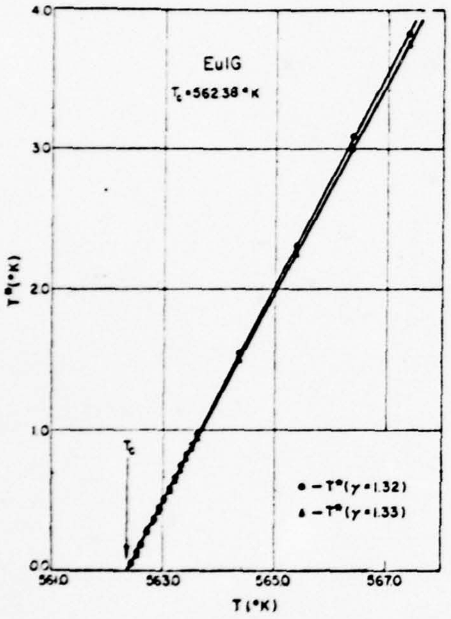


Fig. 5 $T^*(T)$ Versus Temperature for EuIG

SUMMARY AND CONCLUSIONS

The critical exponents for EuIG were determined and found to have the values $\beta = 0.391 \pm 0.001$, $\delta = 4.40 \pm 0.04$, and $\gamma = 1.32 \pm 0.01$. Within the limits of experimental error, the values of the exponents are seen to be consistent with the scaling law prediction $\beta(\delta-1) = \gamma$.

In an attempt to confirm the value of T_c, obtained by application of the kink-point method, we have adopted the technique of Kouvel and Fisher. The results obtained by analyzing our data in terms of this technique clearly show that (1) for the temperature regions considered, the behavior for the magnetic properties of EuIG is accurately described by $\sigma(T) \sim \varepsilon^{\beta}$, for $\varepsilon > 0$ and $\chi_c^{-1} \sim -\varepsilon^{\gamma}$ for $\varepsilon < 0$, since indeed, the functions $T^+(T_t)$ and $T^*(T)$ are linearl dependent upon temperature; (2) the value of T_c, determined by appl ing the Kouvel-Fisher method, is in good accord with the value give by the kink-point method; (3) the kink-point method is a valid approach for obtaining the zero-field mass magnetization in the vicinity of the critical point.

REFERENCES

1. S. Arajs, B. L. Tehan, E. E. Anderson, and A. A. Stelmach, phys. stat. sol. 41, 639 (1970).
2. E. E. Anderson, S. Arajs, A. A. Stelmach, and B. L. Tehan, Physics Department, Clarkson College of Technology Technical Report. No. 1-71 (1971), unpublished.
3. J. S. Kouvel and M. E. Fisher, Phys. Rev. 136, 1626 (1964).
4. B. Widom, J. Chem. Phys. 43, 3898 (1965).
5. L. P.Kadanoff, Physica 2, 263 (1966).
6. R. B. Griffiths, Phys. Rev. 158, 176 (1967).

3

J. Phys. Chem. Solids, 1973, Vol. 34, pp. 1343-1346. Pergamon Press. Printed in Great Britain

MAGNETIZATION OF LUTETIUM IRON GARNET NEAR THE CRITICAL POINT*

A. A. STELMACH, E. E. ANDERSON and S. ARAJS
Clarkson College of Technology, Potsdam, N.Y. 13676, U.S.A.

(*Received* 19 *October* 1972; *in revised form* 20 *December* 1972)

Abstract – A study has been made of the critical magnetic properties of lutetium iron garnet. Values of the critical exponents, β, δ and γ were seen to fulfill the scaling relation, $\beta(\delta-1)=\gamma$, within the limits of experimental error. The critical temperature, obtained from the kink-point plot of applied magnetic field vs break-point temperature, was reaffirmed through utilization of the Kouvel–Fisher analysis.

1. INTRODUCTION

MEASUREMENTS of the magnetic properties of lutetium iron garnet (LuIG) have been made in the vicinity of the Néel temperature. The critical exponents β, δ and γ, which serve to give a description of the behavior of the magnetization, field, and susceptibility, respectively, in the critical region, were evaluated and compared with the scaling theory prediction, $\beta(\delta-1)=\gamma$. Through utilization of the Kouvel–Fisher analysis, it is shown that an accurate method in which to determine the critical temperature involves a plot of applied magnetic field vs break-point temperature whereby the resulting curve is then extrapolated to the zero applied field axis.

2. EXPERIMENTAL RESULTS

To investigate the magnetic behavior of LuIG, measurements were made with a vibrating sample magnetometer on a spherically shaped polycrystalline specimen. The study of the critical exponents was carried out by using the defining equations

$$\sigma(\epsilon,0) \sim \epsilon^{\beta}, \quad \text{for} \quad \epsilon > 0; H_i = 0, \tag{1}$$

$$\sigma(0,H_i) \sim H_i^{1/\delta}, \quad \text{for} \quad \epsilon = 0; H_i \neq 0, \tag{2}$$

and

$$\chi_0^{-1}(\epsilon,0) \sim -(\epsilon^{\gamma}), \quad \text{for} \quad \epsilon < 0; H_i = 0, \tag{3}$$

where $\sigma(\epsilon,0)$ and $\chi_0(\epsilon,0)$ are the zero-field magnetization and susceptibility, respectively, H_i is the internal magnetic field, and ϵ is the reduced temperature, defined by $\epsilon=(T_c-T)/T_c$.

For temperatures immediately below the Néel temperature, T_c, the spontaneous magnetization (see equation (1)) follows a power law behavior. In order to determine this quantity, and hence the critical exponent β, use was made of the kink-point method[1, 2]. In this method, Rayl and Wojtowicz showed that for a given value of the applied field H_a, a magnetic system will undergo a long-range order phase transformation from a state of non-uniform to uniform magnetization. To observe such a thermodynamic phase transformation, one usually takes note of the fact that in a magnetization-temperature plot (at constant applied field), there occurs a kink in the magnetization curve at a temperature denoted by T_t, the break-point temperature. At this temperature, the internal magnetic field vanishes, such that the applied magnetic field is equal to the demagnetization field[3]. Combining this result with equation (1), then leads to an expression of the form

$$H_a(T_t) \sim \epsilon^{\beta}, \quad \text{for} \quad \epsilon > 0; H_i = 0. \tag{4}$$

The variation of the break-point temperature with applied magnetic field for LuIG is shown in Fig. 1. Extrapolation of this curve to the zero applied field axis resulted in a value of

---

*Work supported by the Office of Naval Research under Grant No. N00014-70-A-0000(03).

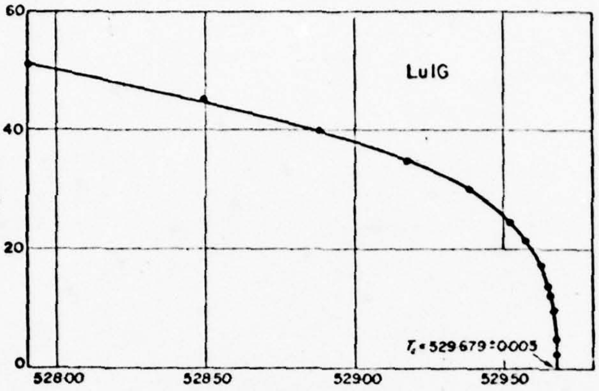


Fig. 1. Applied magnetic field vs break-point temperature for LuIG.

$T_c = 529{\cdot}679 \pm 0{\cdot}005$ K for the Néel temperature. Here the error serves to give an indication of the relative temperature uncertainty in our readings. From a log–log plot of H_a vs $(T_c - T_t)$, a least-square fitted value of $\beta = 0{\cdot}309 \pm 0{\cdot}002$ was obtained in which the linearity of the corresponding curve was valid in the range from $1{\cdot}70 \times 10^{-5} < \epsilon < 9{\cdot}37 \times 10^{-2}$ (Fig. 2).

For the case of $\epsilon = 0$; $H_i \neq 0$, the magnetization is associated with the critical index δ, through the functional relationship of equation (2). In a log–log plot, this expression yielded a least-square value of $5{\cdot}35 \pm 0{\cdot}06$ for the critical exponent δ.

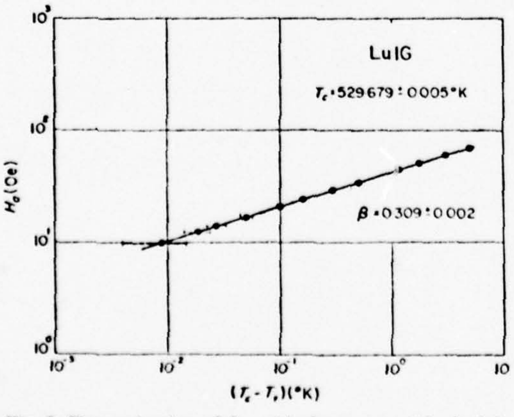


Fig. 2. Determination of the critical exponent β for LuIG.

In the temperature region directly above the critical temperature, the magnetic property of interest is the zero-field susceptibility, χ_0. To determine χ_0 measurements of the magnetization were made as a function of both field and temperature. The data were then graphed in the form of a σ^2 vs H_i/σ plot in which values of χ_0^{-1} were obtained by extrapolation of the isotherms to the H_i/σ axis. From a log–log plot of χ_0^{-1} vs $(T - T_c)$, equation (3) was seen to be satisfied for a least-square value of $\gamma = 1{\cdot}32 \pm 0{\cdot}01$.

Utilizing the assumption of homogeneity in the Gibbs free free energy, scaling theory [4–6] has been able to show that the critical magnetic exponents β, δ and γ are correlated by an expression of the form

$$\beta(\delta - 1) = \gamma. \tag{5}$$

From the experimentally determined values of β and δ, the above relation predicts a value of $\gamma = 1{\cdot}34^{+0{\cdot}03}_{-0{\cdot}02}$. Thus, in the case of LuIG, the value of $\gamma = 1{\cdot}32 \pm 0{\cdot}01$ is seen to fullfill this scaling requirement within the limits of experimental uncertainty.

To test the validity of the value for T_c obtained by use of the kink-point approach, our data was reexamined in terms of a scheme developed by Kouvel and Fisher[7]. A similar analysis has been applied in the case of the europium iron garnet and nickel–copper alloy systems[8–9]. In this technique, a determination is made of the quantities $T^+(T_t)$ and $T^*(T)$ by use of the defining equations

$$T^+(T_t) \equiv \left[H_a\frac{\mathrm{d}}{\mathrm{d}T_t}(H_a^{-1})\right]^{-1}, \text{for } T < T_c \quad (6)$$

and

$$T^*(T) \equiv \left[\chi_0\frac{\mathrm{d}}{\mathrm{d}T}(\chi_0^{-1})\right]^{-1}, \text{for } T > T_c. \quad (7)$$

On assuming equations (1) and (3) to give an accurate description of the behavior for the magnetization and susceptibility in the critical regime and by considering the limiting cases of T_t and T approaching T_c, these equations then reduce to the functional forms, namely

$$T^+(T_t) = \frac{1}{\beta}(T_c - T_t), \text{for } T < T_c \quad (8)$$

while

$$T^*(T) = \frac{1}{\gamma}(T - T_c), \text{for } T > T_c. \quad (9)$$

Using a computer-differentiation program, which consisted of taking a least squares polynomial fit (of second and third order) on sets of 3–5 adjacent experimental points in order to calculate an average derivative, a determination was made of $T^+(T_t)$ and $T^*(T)$ from plots of H_a^{-1} vs T_t and χ_0^{-1} vs T. As seen in Figs. 3 and 4, a value of $T_c = 529{\cdot}7$ K was obtained by extrapolating the linear curves to the zero $T^+(T_t)$ and $T^*(T)$ axes in the plots of $T^+(T_t)$ vs T_t and $T^*(T)$ vs T. The value of T_c is seen to be in good accord with the result obtained from the kink-point plot of H_a vs T_t.

3. SUMMARY AND CONCLUSIONS

The critical exponents for LuIG were measured and found to have the values $\beta = 0{\cdot}309 \pm 0{\cdot}002$, $\delta = 5{\cdot}35 \pm 0{\cdot}06$, and $\gamma = 1{\cdot}32 \pm 0{\cdot}01$. Within experimental uncertainty, the values of the indices are consistent with the scaling equation, $\beta(\delta - 1) = \gamma$.

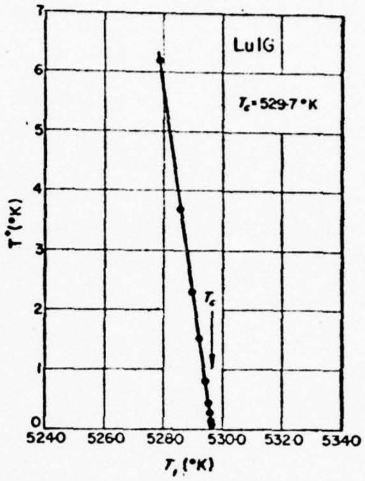


Fig. 3. $T^+(T)$ vs break-point temperature for LuIG.

A Néel temperature of $529{\cdot}679 \pm 0{\cdot}005$ K for LuIG was obtained by application of the kink-point method. Confirmation of this value, made by utilizing the Kouvel–Fisher technique, showed that (1) for the temperature regions immediately below and above T_c, the behavior for the zero-field magnetization

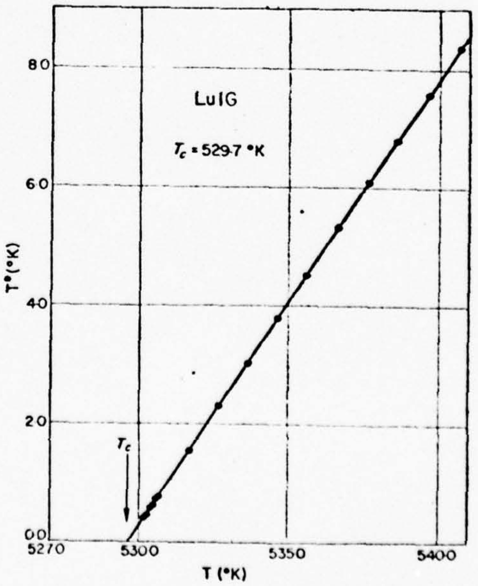


Fig. 4. $T^*(T)$ vs temperature for LuIG.

and susceptibility, respectively, is appropriately described by the power law relations of equations (1) and (3); (2) the value of T_c, obtained from the Kouvel–Fisher plots of $T^+(T_t)$ and $T^*(T)$ vs temperature, is in excellent agreement with the result obtained by the kink-point method.

REFERENCES

1. WOJTOWICZ P. J. and RAYL M., *Phys. Rev. Lett.* 20, 1489 (1968).
2. RAYL M. and WOJTOWICZ P. J., *Phys. Lett.* 28A, 142 (1968).
3. The transition that occurs at T_t is a *finite-field* transition in which the system undergoes a thermodynamic transformation from a state of one mode of long-range order into a state of a different mode of long-range order. This transition should not be confused with the *zero-field* transition which occurs at the critical temperature T_c. Here the system changes from a state of long-range order to a state of short-range order (i.e. at T_c, the long-range order vanishes in zero field).
4. WIDOM B., *J. chem. Phys.* 43, 3898 (1965).
5. KADANOFF L. P., *Physics* 2, 263 (1966).
6. GRIFFITHS R. B., *Phys. Rev.* 158, 176 (1967).
7. KOUVEL J. S. and FISHER M. E., *Phys. Rev.* 136, 1626 (1964).
8. STELMACH A. A., ANDERSON E. E., TEHAN B. L., ARAJS S. and REMEIKA J. P., *Proc. 17th Magnetism Conference*, Chicago (1971).
9. ANDERSON E. E., ARAJS S., STELMACH A. A. and TEHAN B. L., Physics Department, Clarkson College of Technology Technical Report No. 1-71 (1971), unpublished.

4

Int. J. Magnetism
1973, Vol. 4, pp. 173–174

SHORT COMMUNICATIONS

The Critical Exponents β and δ of Yttrium Iron Garnet

S. ARAJS, A. A. STELMACH, and E. E. ANDERSON

Department of Physics, Clarkson College of Technology, Potsdam, New York 13676

(Received January 23, 1973)

The critical exponents $\beta = 0.390 \pm 0.007$ and $\delta = 4.46 \pm 0.03$ have been determined for a single crystal of yttrium iron garnet using magnetization data obtained by means of a vibrating sample magnetometer. The Kadanoff scaling law $\gamma = \beta(\delta - 1)$ predicts that $\gamma = 1.35 \pm 0.04$, which is in good agreement with the measured values of γ by several investigators.

INTRODUCTION

A set of critical phenomena, which has received considerable theoretical and experimental attention, is the behaviour of the static magnetization below and above the critical point, T_c. The following power laws describe such magnetic behaviour:

$$\sigma_s(T) = A\varepsilon^{\beta} \tag{1}$$

$$\chi_0(T) = B\varepsilon^{-\gamma} \tag{2}$$

$$\sigma(H_i, T_c) = CH_i^{1/\delta}, \tag{3}$$

where $\sigma_s(T)$ is the spontaneous mass magnetization, $\chi_0(T)$ is the initial mass magnetic susceptibility, T the absolute temperature, and $\sigma(H_i, T_c)$ is the mass magnetization at T_c. The quantity H_i is the internal magnetic field:

$$H_i = H_a - D\rho(T)\,\sigma(H_i, T), \tag{4}$$

where H_a is the applied magnetic field, D the demagnetizing factor, $\rho(T)$ the density, and $\sigma(H_i, T)$ the mass magnetization at T. The quantities A, B, and C are constants. The symbol ε is defined by

$$\varepsilon = |1 - T/T_c|, \tag{5}$$

and β, δ, γ are exponents which according to Kadanoff[1] should satisfy the equation

$$\gamma = \beta(\delta - 1). \tag{6}$$

The purpose of this paper is to present new magnetization measurements on yttrium iron garnet (YIG) in order to determine β and δ and hence to calculate the exponent γ, which has been measured experimentally by different investigators.[2–5]

EXPERIMENTAL CONSIDERATIONS

The YIG sample used in this study was a sphere of about 1/8 inch in diameter. The magnetization measurements were made by means of a vibrating sample magnetometer using techniques described before.[6]

RESULTS AND DISCUSSION

The critical exponent β of YIG was determined by using equation (1) in conjunction with the kink-point locus approach.[7–8] For applied field values between 2.1 and 80.1 Oe, corresponding break-point temperatures were obtained from magnetization versus temperature plots. From a graph of H_a vs T_t (Figure 1), where T_t is the break-point temperature, the Néel temperature $T_c = 550.494 \pm 0.005$ K was obtained by extrapolation of this field curve to the zero applied field axis. This value of T_c is correct only in the relative sense. From an absolute viewpoint, the value of T_c must be reported as 550.49 ± 0.03 K, which is in excellent agreement with $T_c = 550.41 \pm 0.02$ K determined recently by Berkner and Litster,[5] who used the Faraday rotation of laser light to measure the magnetization of a single crystal of YIG. A log-log plot of H_a vs $(T_c - T_t)$ was found to

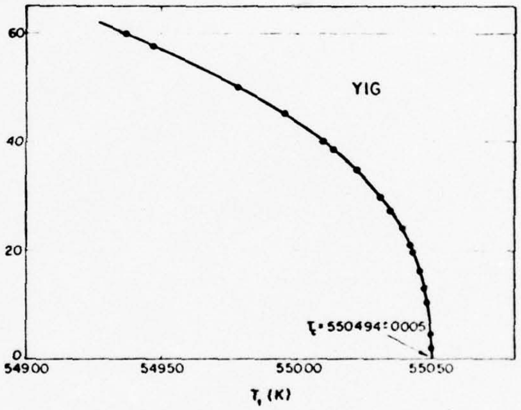


FIGURE 1 Applied magnetic field versus break-point temperature for YIG.

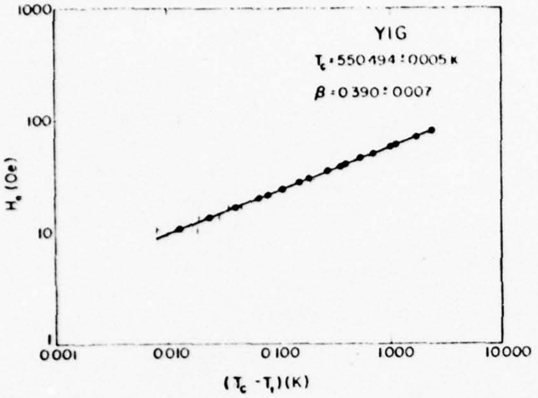


FIGURE 2 Determination of the critical exponent β for YIG.

be linear in the range of $2.36 \times 10^{-5} < \varepsilon < 4.32 \times 10^{-2}$, giving $\beta = 0.390 \pm 0.007$ (Figure 2). It is believed now that the previously observed[9] two values of β, namely $\beta = 0.47$ close to T_c (within 1 K) and $\beta = 0.36$ for the temperature region from 1 to 120 K below T_c, resulted from an improper application of the kink-point method to the experimental data. This subject has been recently discussed with respect to β for nickel.[10] The other previous determinations of β are all single-valued. According to Ohbayashi and Iida,[3] who used a vibrating sample magnetometer for their magnetization studies, $\beta = 0.35 \pm 0.02$ for a single crystal of YIG. A more recent investigation by Miyatani and Yoshikawa,[4] also on a single crystal sample and employing the vibrating sample magnetometer technique, gave $\beta = 0.380 \pm 0.005$.

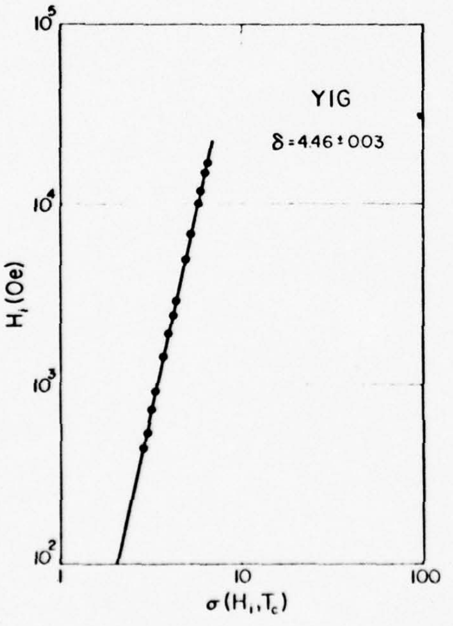


FIGURE 3 Determination of the critical exponent δ for YIG.

The critical exponent δ for our sample of YIG was determined from a log-log of H_i vs $\sigma(H_i, T_c)$ as shown in Figure 3. A least-square analysis gave $\delta = 4.46 \pm 0.03$ which should be compared with the previous measurements by Ohbayashi and Iida[3] ($\delta = 4.6 \pm 0.2$), Miyatani and Yoshikawa[4] ($\delta = 4.42 \pm 0.05$), and Berkner and Litster[5] ($\delta = 4.65 \pm 0.10$).

Assuming the applicability of the scaling law given by equation (6), we can calculate γ from our measurements of β and δ. We find that $\gamma = 1.35 \pm 0.04$. This value is in good accord with previously determined values of γ: 1.30 ± 0.03 (Ref. 2), 1.32 ± 0.04 (Ref. 3), 1.312 ± 0.008 (Ref. 4), 1.35 ± 0.02 (Ref. 5). Thus, it appears that the Kadanoff scaling equation is satisfied by the experimental data of YIG.

ACKNOWLEDGEMENT

The authors are grateful to the Office of Naval Research for their financial support which made this work possible.

REFERENCES

1. L. P. Kadanoff, *Physics* **2**, 263 (1966).
2. K. P. Belov, E. V. Talalaeva, and G. A. Yarkho, *Soviet Phys. JETP* **25**, 989 (1967).
3. K. Ohbayashi and S. Iida, *J. Phys. Soc. Japan* **25**, 1187 (1968).
4. K. Miyatani and K. Yoshikawa, *J. Appl. Phys.* **41**, 1272 (1970).
5. D. D. Berkner and J. D. Litster, Proc. 18th Magnetism Conference, Denver, 1972.
6. S. Arajs, B. L. Tehan, E. E. Anderson, and A. A. Stelmach, *Phys. Stat. Sol.* **41**, 639 (1970).
7. P. J. Wojtowicz and M. Rayl, *Phys. Rev. Letters* **20**, 1489 (1968).
8. M. Rayl and P. J. Wojtowicz, *Phys. Letters* **28A**, 142 (1968).
9. E. E. Anderson, H. J. Munson, S. Arajs, A. A. Stelmach, and B. L. Tehan, *J. Appl. Phys.* **41**, 1274 (1970).
10. E. E. Anderson, S. Arajs, A. A. Stelmach, B. L. Tehan, and Y. D. Yao, *Phys. Letters* **36A**, 173 (1971).

5 22-28 August, 1973, Moscow, USSR, Vol. VI, p. 214 (Publishing House "Nauka", Moscow, USSR, 1974)

NÉEL TEMPERATURES AND ANOMALIES IN ELECTRICAL TRANSPORT PROPERTIES OF ANTIFERROMAGNETIC BINARY CHROMIUM ALLOYS

Sigurds Arajs and Elmer E. Anderson
Department of Physics, Clarkson College of Technology,*
Potsdam, New York 13676, U.S.A.

K. V. Rao and H. U. Åström
Department of Solid State Physics, Royal Institute of Technology,
Stockholm, Sweden

During the last eight years we have extensively studied the electrical resistivity and, to some extent, the thermopower of binary Cr alloys containing elements which can be dissolved in Cr in amounts of at least 0.5 at.%. The motivation for such investigations stems from the uniqueness of the itinerant electron antiferromagnetism in these metallic systems.

Pure Cr below the Néel temperature (T_N = 312 K), possesses a spin-density wave structure which is believed to result from the peculiar shapes of the electron and hole Fermi surfaces. When the electron surface is shifted by a wave vector of magnitude $(\frac{2\pi}{a})$ (0.95,0,0) at absolute zero, where a is the lattice constant of Cr, considerable nesting occurs between large portions of the electron and hole Fermi surfaces. The Coulomb interaction between the electrons and holes associated with this almost perfect nesting is the major cause of the antiferromagnetism of chromium. It can be expected that the Fermi surface structure would change when some other element is dissolved in the Cr lattice. Changes in the Fermi surface should result in changes in various physical properties. Since the electrical resistivity and the thermopower of Cr are quite sensivitve to its magnetic state, those physical quantities are convenient variables to measure as a function of temperature and composition in order to gain further information on the properties of chromium alloys.

Recently [1] we have determined T_N of Cr alloys containing Aℓ, Co, Ge, Ir, Fe, Mo, Ni, Nb, Os, Ru, Si, Ta, Ti, W, and V using the $d\rho/dt$ method. These results show that certain solutes can either increase or decrease T_N of pure Cr considerably. According to the available experimental information, Ti decreases T_N more effectively than any other solute (∿172 K/at.%). On the other hand, small concentrations (below 1 at.%) of Os and Ru in Cr rapidly increase T_N. These particular observations are consistent with predictions based on the simple theory of Fedders and Martin [2]. Other solutes used by us which behave more or less as expected from this viewpoint are Mo, Nb, Ta, W, V, and possibly Si and Ge. The solute Ir exhibits an anomaly, i.e., the T_N vs. c curve possesses a small minimum somewhere below 0.5 at.% level. Higher Ir concentrations, however, produce a normal increase in T_N. The effect of Aℓ on T_N is also complicated, giving rise to a minimum at ∿1.2 at.%. The effect of Co is even more complicated in that a minimum at ∿1.5 at.% is followed by a broad maximum at ∿3.1 at.%. The influence of Fe, Co, and Ni is also anomalous because these metals decrease T_N in spite of the increased electron-atom ratio. Other considerations (existence of localized moments, etc.) not included in the Fedders-Martin theory may be the cause for these deviations.

In general, when a transition metal, other than Fe, Co, and Ni, is dissolved in Cr, the change in ρ and also the absolute thermopower, S, can be understood from the following considerations. For pure Cr the small increase in ρ, when the antiferromagnetic state is reached, results from the combined effects of annihilation of mutually nested electron and hole surfaces and the associated increase in the scattering relaxation time. Since these changes give opposite effects on ρ, the resulting increase in ρ is small. If the transition element added to Cr lattice is on the right hand side of Cr in the periodic chart of atoms, the incommensurable structure is eventually destroyed with increasing solute content giving rise to a commensurable antiferromagnetic state. According to our transport property studies, it appears that when Cr alloys possess this structure the magnetic superzone boundaries have the dominating effect on the nature of ρ below T_N. The resulting ρ anomaly is large. Experimental data with Ru, Os, and Ir clearly support this idea. For example, the onset of commensurable antiferromagnetism in Cr-8.3 at.% Ru alloy increases ρ by ∿57%. On the other hand, if transition metals from the left hand side of Cr are added to Cr lattice, the incommensurable structure is retained, and, in general, the anomalies in ρ are much smaller.

The effects due to nontransition elements such as Si, Ge, and Aℓ are quite different from those described above. For example, Aℓ behaves as a transition metal on the right hand side of Cr because of the existence of a commensurable state above ∿1.5 at.% content. However, the associated anomalies in ρ at T_N are extremely small. The role of Fe and Co, and to some extent Ni, on ρ of Cr is also considerably more complicated than that due to the other transition metals.

In general, large (small) changes in ρ at T_N are accompanied by large (small) changes in S. This is approximately true for dilute (up to ∿3 at.%) Cr alloys containing the following solutes studied so far: Fe, Mo, Ru, Si, W. Higher concentrations cause a deviation in this correlation, i.e., the effects on S diminish much faster than on ρ. A useful quantity for characterizing the effect of the onset of a particular antiferromagnetic state on S is ΔS, which is the difference between the maximum value of S in the antiferromagnetic region (where the antiferromagnetic ordering is nearly complete) and the extrapolated thermopower value from the paramagnetic region at the same temperature. Similarly, we can define a quantity $\Delta\rho$ which represents the electrical resistivity change due to the transition to antiferromagnetism. We find that our data for ΔS and $\Delta\rho$ approximately satisfy the equation

$$\Delta E_g = \frac{\pi^2 K^2 T}{3e} \frac{\Delta\rho}{\rho} \frac{1}{\Delta S} ,$$

where ρ is the total electrical resistivity at the absolute temperature T, K is the Boltzmann constant, e the electric change, and E_g the value of the energy gap formed due to the antiferromagnetic state. We find that the gaps for the commensurable binary chromium alloys are larger (~0.4 eV or less) than those for the incommensurable alloys (~0.1 eV) in good agreement with the direct experimental determinations by Barker and Ditzenberger [3], and Bos et al. [4].

Literature

1. S. Arajs, K V. Rao, H. U. Åström, and T. F. DeYoung, Phys. Scripta (accepted for publication).
2. P. A. Fedders and P. C. Martin, Phys. Rev. 143, 245 (1966).
3. A. S. Barker, Jr. and J. A. Ditzenberger, Phys. Rev. B1, 4378 (1970).
4. L. W. Bos, D. W. Lynch, and J. L. Stanford, Phys. Letters 30A, 17 (1969).

* Work supported by the U. S. Office of Naval Research under grant number N00014-70-A-0311.

6

Volume 45A, number 3 PHYSICS LETTERS 24 September 1973

FIRST ORDER PHASE TRANSITION IN THE MAGNETIC SUSCEPTIBILITY OF Cr–1.37 at%Si

L. HEDMAN, K. SVENSSON, K.V. RAO and S. ARAJS*

Department of Solid State Physics, Royal Institute of Technology, Stockholm, Sweden

Received 8 August 1973

A sharp, first-order change in the magnetic susceptibility of Cr–1.37 at% Si has been found at 238 ± 2 K. It is suggested that this temperature is the Néel temperature and that the transition is from the paramagnetic to the commensurate antiferromagnetic state.

Previous electrical resistivity (ρ) [1], and thermoelectric power (S) [2] studies on Cr-rich Cr-Si alloys have clearly indicated that the effect of Si on the magnetic phase transition of Cr is quite unusual in comparison with the transition metal solutes. Small (up to 1 at%) additions of Si to chromium cause a rapid (~ 84 K/at%) decrease of the Néel temperature (T_N) of chromium. The associated behaviour of ρ in the neighbourhood of T_N in these solid solutions is of the conventional chromium type. However, when the Si concentration slightly exceeds ~ 1 at% level interesting abrupt changes show up in the corresponding ρ versus T and S versus T curves. Specifically, the alloy containing 1.37 at% Si possesses two anomalies in the ρ versus T curve: one of the Cr-type at 110 K and another step-type anomaly at 240 K. The alloys with 1.85 and 2.74 at% Si concentrations also exhibit similar abrupt changes in the ρ versus T curves but show no evidence for any Cr-type anomalies in the transitions. Up to this time the origin of the step-type anomalies in the electrical transport property curves of Cr–Si alloys have not been understood. Because of the unusual behaviour of Si in the chromium lattice, we decided to investigate the nature of these transitions further. Specifically, it seemed to be of interest to explore the magnetic properties in the temperature region where the above mentioned step-type anomalies have been observed. In this letter we report detailed and sensitive magnetic susceptibility (χ) measurements on Cr–1.37 at% Si alloy between 225 and 245 K.

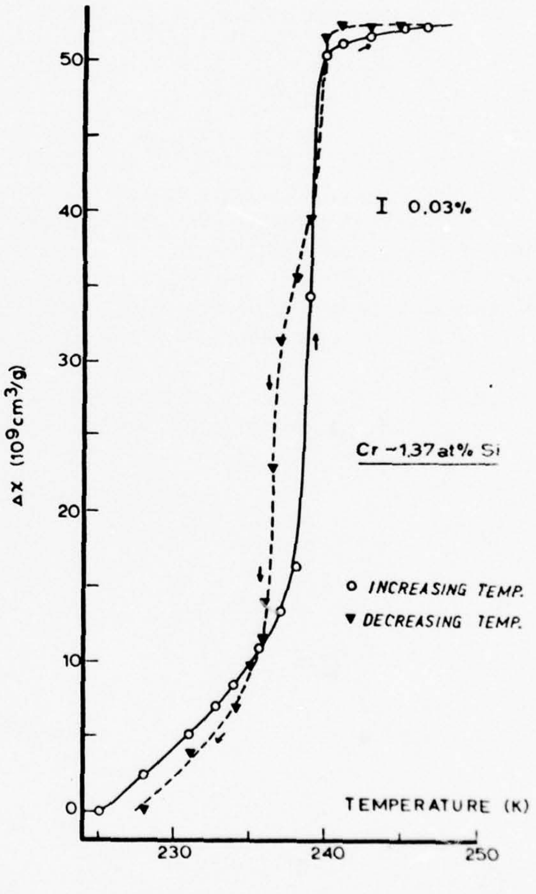


Fig. 1. Changes in the magnetic susceptibility of Cr–1.37 at% Si., between 225 and 245 K.

---

* Visiting Professor, Department of Physics, Clarkson College, of Technology, Potsdam, N.Y., USA.

The sample of mass 0.3 g, whose χ was measured, was cut from the same ingot which was used for the previous electrical transport property studies [1, 2]. The χ measurements were made by the Faraday method ($HH' = 11.04 \times 10^6$ Oe^2/cm), using the Cahn RG automatic electrobalance. In order to obtain the data with a high relative precision, which in our case is of the order of 1 part in 10 000 (0 0.1%), the susceptibility data were taken as a function of temperature keeping the magnetic field constant, the procedure being repeated for different fields. This method eliminates the uncertainties involved in the conventional way of measuring χ as a function of field at fixed temperatures. The quantity χ was measured with increasing and decreasing temperatures using the rate of ~ 1 K/min, in both cases. The experimental results presented as changes $\Delta\chi$, in the χ with respect to the χ value at the beginning of the warming run at 225 K. are shown in fig. 1. One can clearly see from this plot that there is a sharp change in χ at 238 ± 2 K. The small hysteresis effects, associated with the warming and cooling processes are of the same type and magnitude as those seen in the ρ studies. These χ measurements clearly confirm that this transition in the Cr–1.37 at% Si sample is of magnetic origin and strongly suggest that the phase transition is of the first order. It is interesting to note that the over-all behaviour of $\Delta\chi$ versus T of this alloy is very similar to the recently measured first-order change in χ of MnO at its $T_N = 115$ K [3]. Thus our χ studies on Cr–1.37 at% Si sample imply that the phase transition of 238 ± 2 K is a first-order transformation from the paramagnetic state to the commensurable antiferromagnetic state.

In the light of the present investigation, we would like to suggest that the lower temperature anomaly in the ρ versus T curve (1) for the Cr–1.37 at % Si sample at 110 K is possibly associated with a transition from the commensurate antiferromagnetic to the transverse spin density wave structure.

Much more extensive work on new alloys using magnetic and electrical transport studies are needed for a complete elucidation of the magnetic phase diagram of Cr-rich Cr-Si alloys. Such work is in progress.

We are most obliged to Prof. H.U. Åström for his keen interest and encouragement in this work. Technical assistance from L. Khlaif is acknowledged with pleasure. One of us (S. Arajs) wishes to acknowledge with pleasure the kind hospitality of the Chairman and the members of the Solid State Department during stay at Stockholm

This work is supported by grants from Statens Naturvetenskapliga Forskningsråd.

References

[1] S. Arajs and W.E. Katzenmeyer, J. Phys. Soc. Japan 23 (1967) 932.
[2] S. Arajs, E.E. Anderson and E.E.Ebert, Nuovo Cim. 4B (1971) 40.
[3] D. Seino, S. Miyahara and Y. Noro, Phys. Lett. 44A (1973) 35

MAGNETIC PROPERTIES OF Gd-RICH Gd-Sm ALLOYS*

Sigurds Arajs, D. L. Adour, E. E. Anderson, T. F. DeYoung
and K. V. Rao
Department of Physics, Clarkson College of Technology
Potsdam, New York 13676

ABSTRACT

Ferromagnetic Curie temperatures (T_c) of Gd alloys containing 5, 10, 20, 25, 30, and 35 at.% Sm have been determined using the $d\rho/dT$ method, where ρ is the electrical resistivity. It has been found that this technique is consistent with the kink-point method and conventional magnetization vs internal field extrapolations. The effect of Sm on T_c of Gd is nonlinear, the initial decrease (up to about 5 at.% Sm) being only 0.4 K/at.Sm. The decrease in the mass magnetization of the ferromagnetic alloys due to the addition of Sm in Gd is qualitatively similar to the T_c vs concentration dependence.

INTRODUCTION

It is well-known that the interesting magnetic structures of the rare earth metals are formed by the spin and orbital angular momenta of the approximately-localized 4 f electrons. Although the detailed arrangements of the magnetic moments of most of the rare earth metals have been established for some time, the structure of Sm has been determined only recently.[1] According to the magnetic susceptibility and electrical resistivity studies,[2] polycrystalline Sm exhibits two magnetic transitions: one at about 14 K and another at 106 K. Koehler and Moon,[1] using neutron-diffraction studies, have determined that the low temperature transition is associated with the ordering of the magnetic moment on the hexagonal sites, while the high temperature one is due to the ordering on the cubic sites. Because of the existence of these unique magnetic structures in pure Sm and due to the fact that practically nothing is known about the magnetic properties of binary Sm alloys, we have initiated extensive investigations of the physical properties of Sm alloys with other rare earth elements. In this paper we report the results of magnetic and transport property measurements of Gd-rich Gd-Sm alloys.

SAMPLES AND APPARATUS

The polycrystalline samples of Gd-Sm used in this investigation were prepared by the method of arc-melting using the facilities described elsewhere.[3] The stocks of pure (distilled) samarium and gadolinium (both of 99.9% purity) were purchased from Research

---

* Work supported by the Office of Naval Research under grant number N0014-70-A-0311-0001-05.

hemicals. From the homogenized (at 1150 K for 170 hours) single- hase ingots weighing about 20 g, samples were prepared in the form f spheres (dia. ~ 3 mm) and parallelepipeds (~25 mm x 4 mm x 4 mm). he spheres were used for the measurements of the magnetic moments y means of the PAR vibrating sample magnetometer associated with he Magnion 15-in. electromagnet.[4] Various temperatures between 7 and 300 K were obtained and controlled using an Andonian Dewar pecifically designed for the vibrating sample magnetometer and AR Cryogenetic Temperature Controller (Model 152). The parallele- ipeds were used for the electrical resistivity studies. These easurements were carried out between 4.2 and 310 K by means of the quipment described earlier.[5]

EXPERIMENTAL RESULTS

One of the physical quantities which characterizes a binary agnetic system is the composition dependence of some particular agnetic transition. Gd is the simplest of all the magnetically- rdered rare earth metals,[6] possessing the Curie temperature $_c$ = 293.3 ± 0.1 K.[7] When Sm is added to Gd, it can be expected hat T_c would decrease. Experimentally, we have found that this, ndeed, is the case. From our studies of the electrical resistivity ρ) and the behavior of the magnetization (σ) at low applied fields, e have found that either the method of the first derivative of the lectrical resistivity (dρ/dT) or the kink-point method[8,9] is a good echnique for the determination of T_c of Gd alloys. Figure 1 shows the plots of dρ/dT vs T, calculated by means of a computer, for Gd-Sm alloys containing 5, 10, 20, 25, 30, and 35 at.% Sm in the neighborhood of their respective Curie temperatures. The exact location of T_c is shown by arrows. Figure 1 clearly reveals that the temperature variation of ρ around T_c is very similar in all Gd-rich alloys containing various amounts of Sm. It appears that T_c can be determined reliably within at least a few degrees from the dρ/dT vs T plots by finding the temperature where dρ/dT exhibits a minimum, which becomes more pronounced in alloys of higher Sm concentration. In the 5 at.% Sm alloy the minimum disappears and we chose T_c at the point where the slope of dρ/dT changes abruptly (see Fig. 1). This method of the determination of T_c is supported by the kink-point and conventional magnetization studies. A typical plot of the mass magnetization (σ) as a function of T in low applied fields is shown in Fig. 2, where the data are presented for the spherical sample containing 5 at.% Gd. Although the transitions from the nonuniform to the uniform magnetization (the kink-point) are not as sharp in alloys as in pure substances, the values of T_c still can be clearly determined from such plots. In general, the determination of T_c from the kink-point data are in good agreement with the resistivity data as mentioned above. Furthermore, we also have examined the conventional σ vs T plot associated with low (a few hundred Oe) internal fields. The values of T_c estimated from these curves, (although a less accurate technique) are also in reasonable greeement with the dρ/dT and kink-point determinations.

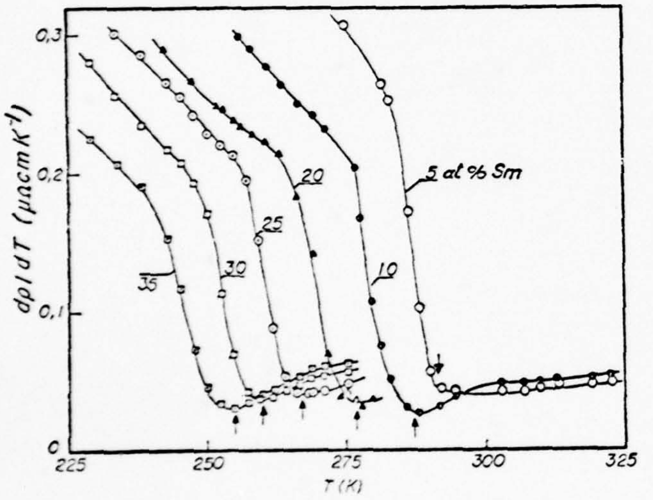


Fig. 1. Temperature derivatives of the electrical resistivity of Gd-Sm alloys in the neighborhood of their Curie temperatures.

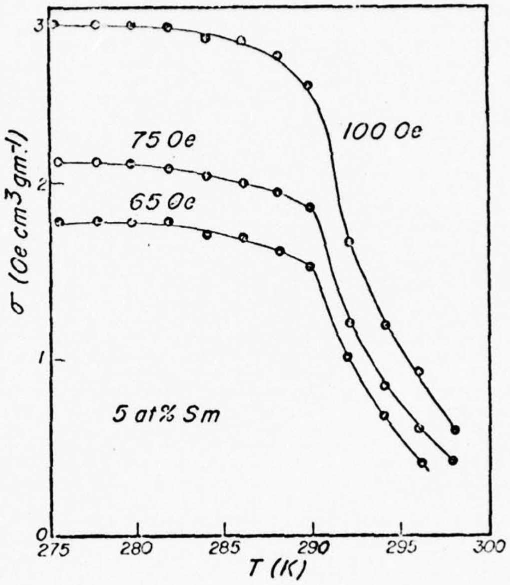


Fig. 2. Kink-point plot for Gd 5 at.% Sm alloy.

The dependence of T_c on Sm concentration (c) is shown in Fig. 3. The decrease in T_c is about 0.4°K/at.% Sm up to 5 at.%Sm; for larger concentration, T_c decreases more rapidly. The decrease in the mass magnetization at constant temperature (for example, 250 K) and constant internal field (~10 KOe) as a function of c behaves (not shown in this paper) in a similar fashion up to at least 20 at.% Sm level. It should be remarked that the effects of Sm on Gd are quite different from those of, for instance, Sc and Y. In particular, Nigh et al.,[10] have found that additions of Sc to Gd greater than 25 at.% very rapidly eliminates the ferromagnetic phase giving rise to an antiferromagnetic state. Whether such behavior also takes place in the central portion of the Gd-Sm system is presently under investigation.

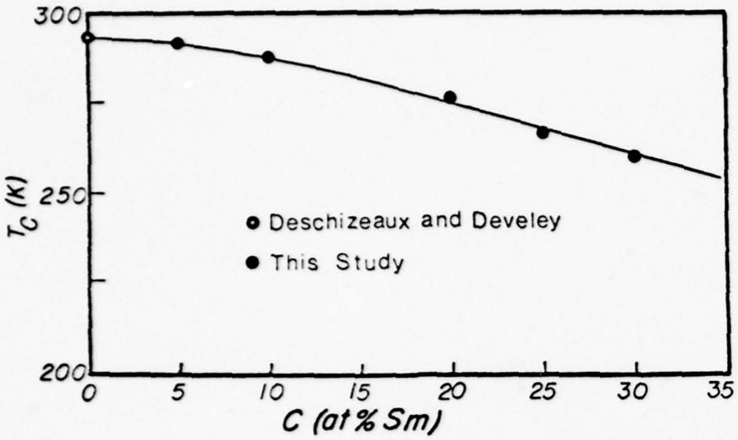


Fig. 3. Curie temperature of Gd-Rich Gd-Sm alloys as a function of Sm concentration.

ACKNOWLEDGMENTS

The authors are thankful to C. D. Levermore and J. R. Kelly for their assistance with computer calculations.

REFERENCES

1. W. C. Kohler and R. M. Moon, Phys. Rev. Letters 29, 1468 (1972).
2. S. Arajs and G. R. Dunmyre, Z. Naturforsch 21a, 1856 (1966).
3. S. Arajs and G. P. Wray, J. Phys. E 2, 518 (1969).
4. S. Arajs, B. L. Tehan, E. E. Anderson, and A. A. Stelmach, phys. stat. sol. 41, 639 (1970).
5. S. Arajs, Canad. J. Phys. 47, 1005 (1969).
6. C. D. Graham, Jr., J. Phys. Soc. Japan 17, 1310 (1962).
7. M. N. Deschizeaux and G. Develey, J. Physique 32, 319 (1971).
8. M. Rayl and P. J. Wojtowicz, Phys. Letters 28A, 142 (1969).
9. E. E. Anderson, S. Arajs, A. A. Stelmach, B. L. Tehan, and Y. D. Yao, Phys. Letters 36A, 173 (1971).
10. H. E. Nigh, S. Legvold, F. M. Spedding, and B. J. Beaudry, J. Chem. Phys. 41, 3799 (1964).

Journal of Low Temperature Physics, Vol. 14, Nos. 5/6, 1974

Spin-Flip Transition in the Chromium–Tungsten System*

L. Hedman, K. Svensson, K. V. Rao,† S. Arajs,‡ and H. U. Åström

Department of Solid State Physics, Royal Institute of Technology, Stockholm, Sweden

(Received September 24, 1973)

The magnetic susceptibility χ of polycrystalline Cr and Cr–0.3 at.% W samples has been studied in the neighborhood of the spin-flip transition T_{sf} with a relative precision of one part in 10^4. In pure Cr, χ exhibits a step-type anomaly at $T_{sf} = 123.0 \pm 0.5$ K. The χ behavior of the Cr–0.3 at.% W alloy is different from that of pure Cr: No step anomaly exists, but at $T_{sf} = 112.5 \pm 0.5$ K $d\chi/dT$ shows a sharp minimum.

Chromium is an itinerant antiferromagnet whose magnetic structure below the Néel temperature, $T_N \approx 312$ K, is made up of static spin density waves (SDW). Between T_N and the spin-flip temperature, $T_{sf} \approx 122$ K, the SDW is transversely polarized, i.e., the wave vector is perpendicular to the spin polarization vector. Below T_{sf} these vectors are parallel and the SDW is longitudinally polarized. When some other element is dissolved in the chromium lattice it is expected that T_N and T_{sf} will change with solute concentration. The composition dependence of T_N can be easily studied by electrical resistivity measurements. Considerable amounts of information have been collected recently in this fashion.[1] However, the electrical resistivity measurements are not useful for the investigation of T_{sf} as a function of the type and concentration of solutes. Therefore very little data exist in this area. It has been noticed in the past[2–4] that the magnetic susceptibility χ undergoes measurable changes at both T_N and T_{sf}. Thus the χ vs. T plots, where T is the temperature, could be used for the determination of the transition temperatures. However, very little work has been done on χ of various dilute chromium alloys at low temperatures. The purpose of this note is to show that T_{sf} of chromium alloys can be determined reliably by sensitive χ measurements.

---

*Work supported by grants from Statens Naturvetenskapliga Forskningsråd.

†Present address: Department of Physics, Clarkson College of Technology, Potsdam, New York.

‡Visiting Professor, Department of Physics, Clarkson College of Technology, Potsdam, New York.

The χ data on chromium and chromium–0.3 at.% tungsten samples in the neighborhood of T_{sf} were made by the Faraday method using the Cahn RG automatic electrobalance with a relative precision of the order of one part in 10^4. The samples, weighing about 0.4 g, were cut by means of the spark erosion method from arc-melted ingots described elsewhere.[5] The chromium–0.3 at% tungsten sample was annealed at 1400°C for 120 h and then slowly cooled to room temperature. The pure chromium specimen was similarly heat-treated at 1000°C. The magnetic susceptibility changes $\Delta\chi$ in the neighborhood of T_{sf} of chromium and chromium–0.3 at.% tungsten alloy are shown in Figs. 1 and 2, respectively. The curves represent the averages of numerous individual runs obtained with either increasing or decreasing temperature. Both warming and cooling runs give essentially the same $\Delta\chi$ vs. T curves, within the experimental accuracy. According to the present study T_{sf} for the pure chromium is 123.0 ± 0.5 K. As can be seen from Fig. 1, $\Delta\chi$ undergoes approximately a step-type anomaly with increasing T at T_{sf}. Such behavior has been observed before by Munday *et al.*[2] and Chiu *et al.*,[4] but not by Bender and Müller,[3] who report a peak in χ at T_{sf}. The plot of χ vs. T for the chromium–0.3% tungsten alloy (Fig. 2) is noticeably different than that for pure chromium. This curve is quite similar to the electrical resistivity curve in the neighborhood of T_N. This can be seen even more clearly in the $d\chi/dT$ vs. T plot shown in Fig. 3. The closed points are

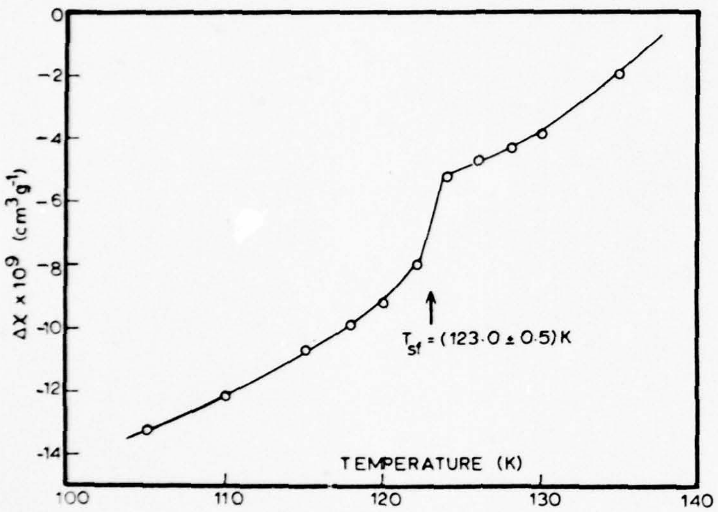


Fig. 1. Magnetic susceptibility changes of chromium in the neighborhood of T_{sf}.

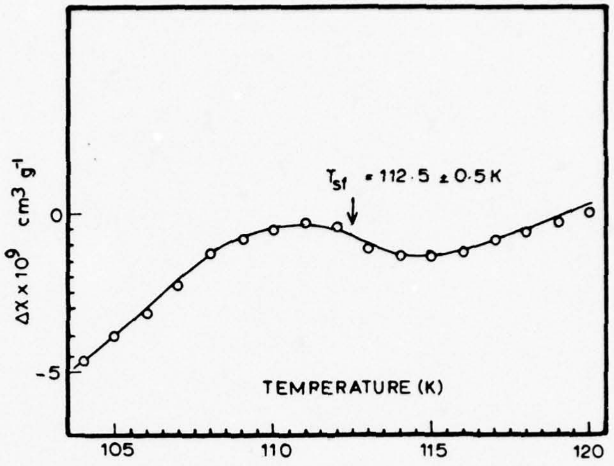


Fig. 2. Magnetic susceptibility changes of chromium–0.3 at.% tungsten alloy in the neighborhood of T_{sf}.

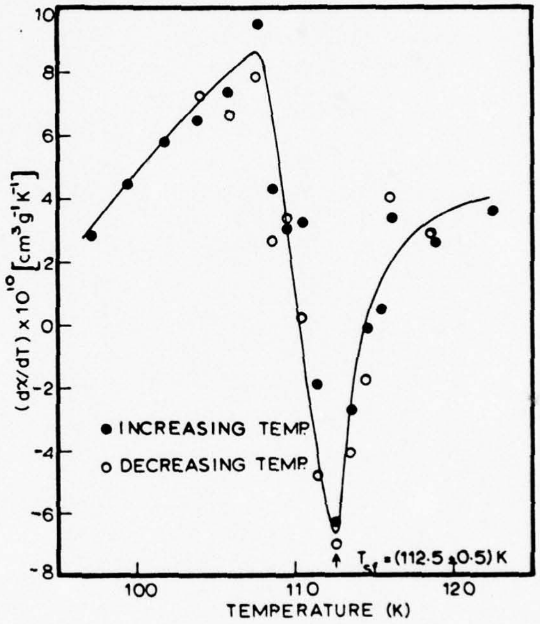


Fig. 3. $d\chi/dT$ of Cr–0.3 at.% W alloy in the neighborhood of T_{sf}.

average values of $d\chi/dT$ associated with warming runs and the open points are those for the cooling runs. At T_{sf} there is a minimum in the $d\chi/dT$ curve. In this manner it is found that $T_{sf} = 112.5 \pm 0.5$ K for the chromium–0.3 at.% tungsten alloy. The only known previous experimental study of T_{sf} as a function of tungsten concentration is due to Koehler *et al.*[6] These investigators, using neutron diffraction methods, found that $T_{sf} = 60$ k for the 1.89 at.% tungsten sample and that $T_{sf} = 4.2$ K for the 3.64 at.% tungsten specimen. The results of this study are in excellent agreement with Koehler *et al.*'s data. The decrease in T_{sf} with tungsten concentration is linear, and the longitudinal SDW is eliminated when the tungsten concentration reaches about 3.8 at.%.

In summary, it seems that the conventional but high-accuracy magnetic susceptibility measurements can be used for the determination of T_{sf} in dilute chromium alloys. It would be of interest to extend studies of this type to other binary chromium systems. Such investigations are being planned in this laboratory.

ACKNOWLEDGMENTS

Technical assistance from L. Khlaif is acknowledged with pleasure. One of us (S.A.) wishes to acknowledge the hospitality of the Chairman and the members of the Solid State Department during his stay in Stockholm.

REFERENCES

1. S. Arajs, K. V. Rao, H. U. Åström, and T. F. Young, *Physica Scripta* **8**, 109 (1973).
2. B. C. Munday, A. R. Pepper, and R. Street, in *Proc. Int. Conf. on Magnetism, Nottingham, England, 1964* (The Institute of Physics and the Physical Society, London, England, 1965), p. 201.
3. D. Bender and J. Müller, *Phys. Kondens. Materie* **10**, 342 (1970).
4. C. H. Chiu, M. H. Jericho, and R. H. March, *Can. J. Phys.* **49**, 3010 (1971).
5. S. Arajs, *J. Appl. Phys.* **39**, 673 (1968).
6. W. C. Koehler, R. M. Moon, A. L. Trego, and A. R. Mackintosh, *Phys. Rev.* **151**, 405 (1966).

9

Journal of Magnetism and Magnetic Materials 1 (1975) 141–143

MAGNETIC SUSCEPTIBILITY STUDIES OF POLYCRYSTALLINE CHROMIUM AND CHROMIUM-0.3 AT.% TUNGSTEN ALLOY IN THE NEIGHBORHOOD OF THE NÉEL TEMPERATURE *

L. HEDMAN and H.U. ÅSTRÖM
Department of S.S.P., Royal Institute of Technology Stockholm, Sweden

and

K.V. RAO and Sigurds ARAJS
Department of Physics, Clarkson College of Technology Potsdam, New York 13676, U.S.A.

Magnetic susceptibility (χ) measurements of the relative precision of 1 part in 10^4 have been made on pure Cr and Cr-0.3 at.% W alloy about 10 K below and above the respective Néel temperatures, T_N. For Cr, $T_N = (311.8 \pm 0.2)$K, and for Cr-0.3 at.% W, $T_N = (305.0 \pm 0.2)$K. Temperature dependence of $d(\chi T)/dT$ above T_N is very sensitive to heat treatments while below T_N the values of $d(\chi T)/dT$ remain the same for Cr-0.3 at.% W sample and approximately the same for pure Cr specimen. Below T_N the critical behavior of Cr and Cr-0.3 at.% W is essentially logarithmic.

1. Introduction

According to neutron diffraction studies [1], the transformation from the antiferromagnetic to the paramagnetic state in a pure chromium single crystal is a first order transition. Experimentally [2], it has been observed that the nature of this transition is very sensitive to impurities, strains, and, in the case of polycrystalline samples, the size of crystallites. Theoretically, for quite a few years, no clear-cut models were proposed which could explain the first order aspects of this transition. Very recently, Young and Sokoloff [3] have provided the possible reasons for the failure of various two band models to give the first order transition. Furthermore, they have demonstrated that using a three band model similar to that studied by Falicov and Penn [4], and including harmonics of spin density waves in their model a first order transition takes place at the Néel temperature, T_N. However, this first order effect being weak, one considers chromium as a system with an interrupted second order phase transition. A careful study of the empirical laws close to the transition in the narrow meaningful region, which, in this case, has a width

$$\epsilon < 10^{-2}, \text{ where } \epsilon = |T - T_N|/T_N,$$

is therefore of considerable interest.

The magnetic susceptibility change in the neighborhood of T_N is very small [5–7]. For this reason no detailed susceptibility studies, from the viewpoint of the critical behavior, have been made as yet. Such investigations, however, have been done for the electrical resistivity [8–12]. The experimental results clearly demonstrate that the determination of various critical indices is a complicated matter because of their sensitivity to the physical state of the samples. From the viewpoint of the critical behavior, the magnetic susceptibility is a simpler physical property than the electrical resistivity since the susceptibility emphasizes the static instead of the dynamic aspects of the phase transition. With these ideas in mind, we decided that it would be of interest to exploit magnetic susceptibility measurements as sensitive probe to explore the behavior of pure chromium and some binary chromium alloy in the neighborhood of T_N. The results of such attempts are briefly described in this communication.

---

* Work supported by grants from Statens Naturvetenskapliga Forskningsrad, Sweden, and Office of Naval Research, USA.

2. Experimental considerations

The magnetic susceptibility of the relative precision of 1 part in 10^4 was determined using the Faraday method briefly described elsewhere [13]. The force measurements were made with a Cahn RG electrobalance having the sensitivity of 0.2 μg. The magnetic field and its gradient was produced by the Sucksmith-type magnetic pole pieces of the 8-inch electromagnet made by Newport Instruments. The electric current was kept constant to within 3 parts in 10^5. The sample, whose magnetic properties were investigated, was attached to the balance by means of tungsten wire (diameter 0.05 mm). The weight of the samples described in this communication was about 0.15 g for Cr and 0.18 g for Cr-0.3 W. The different temperatures, controlled to within ± 0.01 K.

The sample of chromium was cut from an arc-melted ingot by a spark-erosion method. The ingot, prepared from high-purity chromium stock (Chromalloy Corporation), was the same used for previous electrical resistivity studies [14]. The sample containing 0.3 at.% W was cut in a similar fashion from the one used in the electrical resistivity studies described before [15].

3. Results and discussion

If the magnetic susceptibility, χ, near a phase transition obeys a power law with a critical index η^+ or η^-, where the plus sign refers to temperature region above the transition temperature, T_c, and the minus sign below it, then

$$\frac{d(\chi T)}{dT} = A^{\pm} + B^{\pm}\epsilon^{\eta^{\pm}}\text{, where} \qquad (1)$$

the quantities $A^{\pm}$ and $B^{\pm}$ are constants. Thus, from the viewpoint of critical phenomena, it is more convenient to plot $d(\chi T)/dT$ as a function of T than χ vs T. Figures 1 and 2 show such plots for pure Cr and Cr-0.3 at.% W alloy. From these plots it is easy to obtain the Néel temperature for pure Cr to be (311.8 ± 0.2) K and that of Cr-0.3 at.% W alloy (305.0 ± 0.2) K, in good agreement with previous electrical resistivity determinations [15]. The curves in figs. 1 and 2 associated with "as received" state represent measurements done on samples after the spark-cutting from the original arc-melted ingots. The runs labelled as "annealed" were made after these samples were annealed at 1000 C for about 100 hours and then furnace-cooled to room temperatures. It is very obvious from figs. 1 and 2 that the detailed behavior of magnetic susceptibility above T_N for either pure Cr and Cr-0.3 at.% W alloy is very sensitive to the above-described heat treatments. In fact, this sensitivity is such that a meaningful determination of η^+ is impossible. The situation is quite different below T_N. The behavior of $d(\chi T)/dT$ for Cr-0.3 at.% W is the same for the "as received" and "annealed" states and approximately similar for pure Cr under the same treatments. If one makes an assumption that $A^- = 0$, implying the absence of the $1/T$ term in χ, which seems to be a reasonable assumption for Cr and dilute Cr alloys (as confirmed by our plot in fig. 3), then a plot of $\log[d(\chi T)/dT]$ vs $\log|T - T_N|$ should give η^-. This is shown in fig. 3, from which one can clearly see that η^- remains a constant at least for the range of $|T - T_N|$ between 0.8 and 15 K. In fact, numerical calculators give that η^- for "as received" Cr is about 0.03 ± 0.02, for "annealed" Cr 0.05 ± 0.02, and for Cr-0.3 at.% W 0.03

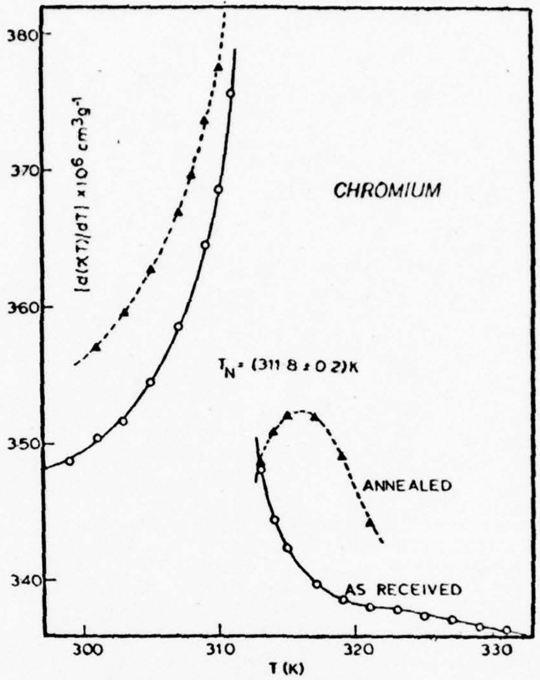


Fig. 1. Temperature derivative of χT of Cr in the neighborhood of T_N.

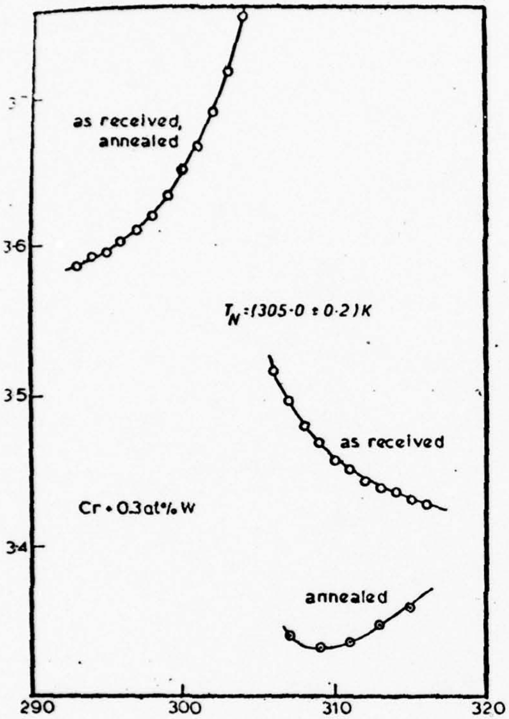
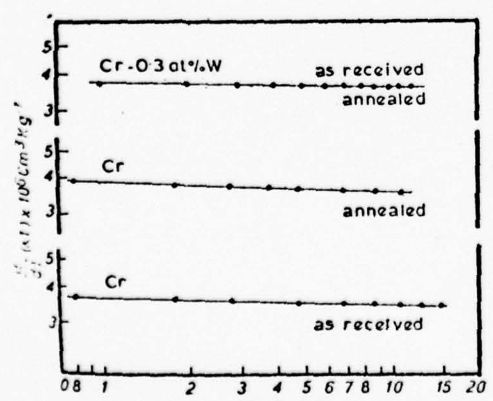


Fig. 2. Temperature derivative of χT of Cr-0.3 at.% W in the neighborhood of T_N.



3. Log $d/dT(\chi T)$ as a function of log $(T-T_N)$ for Cr and 3 at.% W.

± 0.02 in both either "as received" or "annealed" state. These values of η^- strongly suggest that the critical behavior of χ of Cr and likely dilute Cr alloys below T_N is essentially logarithmic. Such a behavior has been predicted theoretically by Dzyaloshinski and Kats [16]. The great sensitivity of χ above T_N resulting from different heat treatments is not clear at the present time, though the observed first order effect must play a role in this. From purely experimental viewpoints, such sensitivity is also exhibited in the critical behaviour of the electrical resistivity above T_N [11,12]. Further work on these matters is in progress.

We thank Lutfi Khlaif for his skillful help in performing some of the measurements, and K. Svensson for valuable technical advice.

References

[1] A. Arrott, S.A. Werner and H. Kendrick, Phys. Rev. Letters 14 (1965) 1022.
[2] G. Benediktsson, "Investigations on the Order of Magnetic Phase Transitions in Cr and some Cr Alloys at the Néel Point". Thesis TRITA-FYS-5011, Dept. of Solid State Physics, Royal Institute of Technology, Stockholm, Sweden.
[3] C.Y. Young and J.B. Sokoloff, AIP Conf. Proc. 18 (1974) 342.
[4] L.M. Falicov and D.R. Penn, Phys. Rev. 158 (1967) 476.
[5] R. Lingelbach, Z. Physik. Chem. 14 (1958) 1.
[6] W.D. Weiss and R. Kohlhaas, Z. Naturforsch. 19a (1964) 1631.
[7] B.C. Munday, A.R. Pepper and R. Street, Brit. J. Appl. Phys. 15 (1964) 611.
[8] E.B. Amitin and Y.A. Kovalevskaya, Soviet Phys. - Solid State 9 (1968) 2145.
[9] G.T. Meaden and N.H. Sze, Phys. Rev. Letters 29A (1969) 162.
[10] M.B. Salamon, D.S. Simons, and P.R. Garnier, Solid State Comm. 7 (1969) 1035.
[11] C. Akiba and T. Mitsui, J. Phys. Soc. Japan 31 (1971) 300; 32 (1972) 644.
[12] O. Rapp, S. Arajs, and K.V. Rao, Critical Behavior of the Electrical Resistivity of Chromium Near the Néel Temperature (to be published).
[13] L. Hedman, K. Svensson, K.V. Rao and S. Arajs, Phys. Letters 45A (1973) 175.
[14] S. Arajs and G.R. Dunmyre, J. Appl. Phys. 36 (1965) 3555.
[15] S. Arajs, J. Appl. Phys. 39 (1968) 673.
[16] I.E. Dzyaloshinski and E.I. Kats, Sov. Phys. JETP. 35 (1972) 584.

MAGNETIC PROPERTIES OF Cr CONTAINING DILUTE CONCENTRATIONS OF Co IN THE NEIGHBORHOOD OF THE NÉEL TEMPERATURE

Sigurds Arajs, E. E. Anderson, Jack R. Kelly, and K. V. Rao
Department of Physics
Clarkson College of Technology
Potsdam, New York 13676

ABSTRACT

Magnetic susceptibility (χ) of Cr and Cr alloys containing 1.7, 2.2, 2.7, 4.4, and 6.2 at.% Co have been measured as a function of temperature (T) between 300 and 600 K. Each of the χ vs T curves exhibits a well-defined maximum at the Néel temperature (T_N). Assuming that χ of the matrix is unchanged by small additions of solute, the magnetic susceptibility of Co (χ_{Co}) in Cr has been determined over the above-mentioned T range. Above T_N (except close to T_N)χ_{Co} obeys the Curie-Weiss law. The magnetic moment per Co atom decreases with increasing Co concentration. It has been found the χ_{Co} just above T_N cannot be described by a power law with constant critical exponents.

INTRODUCTION

Previous experimental studies[1-3] of the magnetic properties of Cr containing Fe, Co, and Ni strongly suggest that there are localized magnetic moments on Fe and Co, but not on Ni atoms. Furthermore, it appears that below the Néel temperature, the localized moments on Co atoms strongly couple with the Cr lattice, while those on Fe atoms interact weakly with the average magnetic moment of Cr. The purpose of this paper is to present new and detailed studies of the magnetic susceptibility in the neighborhood of the Néel temperature and to discuss the significance of the experimental results.

EXPERIMENTAL CONSIDERATIONS

The Cr-Co samples used in this study, containing 1.7, 2.2, 2.7, 4.4, and 6.2 at.% Co, were cut from the specimens used previously[4] for the electrical resistivity investigations. The magnetic susceptibilities were determined using the Faraday method. The magnetic field was produced by a Magnion 7-inch electromagnet with tapered pole pieces in conjunction with a Magnion Model 1050B power supply. Force measurements were made with an Ainsworth Type 15 electrobalance. The signal output from the balance was read on a Hewlett-Packard 3439A digital voltmeter coupled to a 3443A range unit. The overall accuracy of the magnetic susceptibility measurements was ±0.5% with a relative precision of 1 part in 10^4. It was possible to maintain temperatures within ±0.1 K above about 500 K and within ±0.01K at lower temperatures.

RESULTS AND DISCUSSION

The mass magnetic susceptibility, χ, of Cr and Cr-Co alloys is shown as a function of the absolute temperature, T, in Fig. 1. The anomaly in χ for Cr at the Néel temperature, $T_N \approx 312$ K, is very small in comparison with the large peaks at T_N of Cr-Co alloys. Since the sample containing 1.7 at.% Co has T_N below 300 K, there is no maximum in the χ vs T curve as shown in Fig. 1. The usual method of interpretation of χ data on dilute alloys is to assume that χ of the bulk alloy consists of two components, the susceptibility of the matrix, χ_o, and the susceptibility of the solute impurity, χ_{Co}. Furthermore, it is usually assumed that χ_o is unchanged by small additions of Co. Then

$$\chi = w\chi_{Co} + (1-w)\chi_o,$$

where w is the weight fraction of Co. The T dependence of the quantities $1/\chi_{Co}$, calculated from the above equations are shown in Fig. 2. The straight line behavior, except very close to T_N, clearly confirms that there is a localized moment on Co atoms. Table I gives the values of T_N, determined from $d\chi/dT$ vs T plots, the effective paramagnetic moments, μ_{Co}, and the T range over which the Curie-Weiss law has been used for the determination of μ_{eff}.

Our values of T_N are in good agreement with those determined by Booth[3]. According to Suzuki[2] μ_{Co} is 2.9±0.1 μ_B for the Co concentrations between 1 to 6 at.%. Booth[3] finds that μ_{Co} decreases slightly from 2.3±0.4 μ_B at 1.9 at.% Co, and to 2.0±0.2 at 9.3 at.% Co. Our values of μ_{Co} are higher than those found by Suzuki and Booth. Our μ_{Co} values also show a strong decrease with increasing Co concentrations. It should be remarked that Lingelbach[1] expects μ_{Co} to be 3.87 μ_B, which is the approximate value of μ_{Co} if our data are extrapolated to low levels of Co content. Furthermore, according to Fallot,[5] μ_{Co} in metallic Co in the paramagnetic region is 3.1 μ_B. The reasons for the discrepancies between Suzuki, Booth and our results on μ_{Co} are not clear at the present time.

Lastly, we also have examined in detail the paramagnetic behavior of χ_{Co} in the neighborhood of T_N. Plots of $\ln\chi_{Co}$ vs $\ln(T-T_N)$ (which due to space limitations are not shown here) for the samples containing 2.2, 2.7, 4.4, and 6.2 at.% Co, are not straight lines but continuous curves with gradually increasing negative scope as $(T-T_N)$ increases from 1 to 40 K. Thus it is not possible to assign a well-defined critical exponent for χ_{Co} above T_N.

ACKNOWLEDGMENTS

This work has been supported by grant number GH-37908 from the National Science Foundation and by the Office of Naval Research under grant number N0014-70-A-0311-0001.

Table I

T_N and μ_{Co} of Cr-Co Alloys

Co centration (at.%)	T_N(K)	$\mu_{Co}(\mu_B)$	Temperature Range (K)
1.7		3.6	304-425
2.2	312	3.5	348-520
2.7	336	3.4	380-582
4.4	323	3.0	340-584
6.2	317	2.9	340-595

REFERENCES

1. R. Lingelbach, Z. Phys. Chem. 14, 1 (1958).

2. T. Suzuki, J. Phys. Soc. Japan 21, 442 (1966).

3. J. G. Booth, J. Phys. Chem. Solids 27, 1639 (1966).

4. S. Arajs, G. R. Dunmyre, and S. J. Dechter, Phys. Rev. 154, 448 (1967).

5. M. Fallot, J. Phys. Radium 5, 153 (1944).

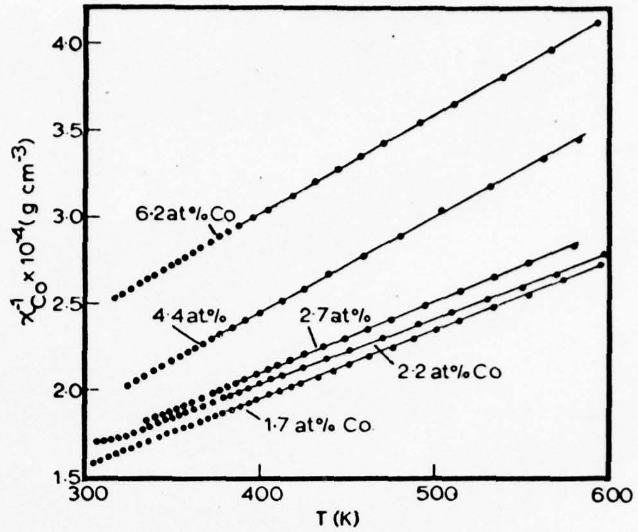


fig.2 χ_{Co} in Cr-Co alloys

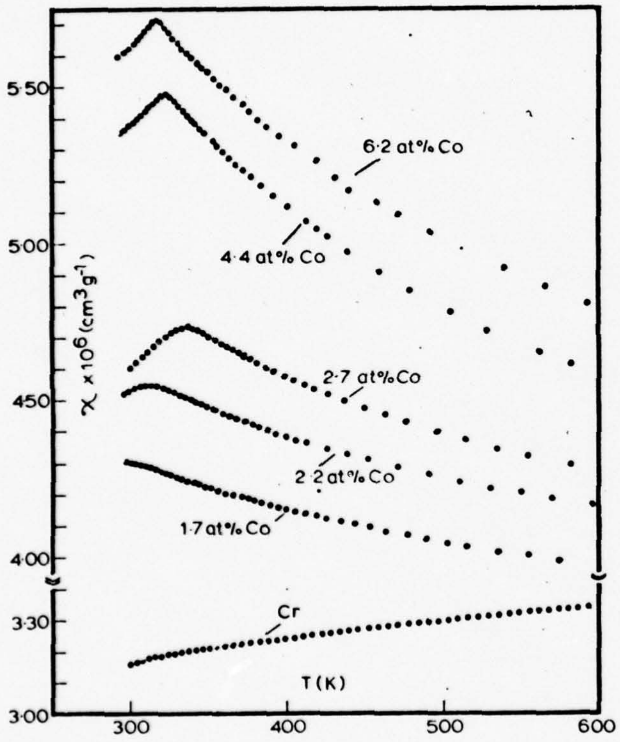


fig.1 χ of Cr-Co alloys

11

Journal of Low Temperature Physics, Vol. 21, Nos. 1/2, 1975

Magnetic Susceptibility of Polycrystalline Samarium Between 4 and 300 K

Sigurds Arajs and K. V. Rao

Department of Physics, Clarkson College of Technology, Potsdam, New York

and L. Hedman and H. U. Åström

Department of Solid State Physics, Royal Institute of Technology, Stockholm, Sweden

(Received March 10, 1975)

Magnetic susceptibility χ of polycrystalline rhombohedral samarium has been measured as a function of temperature T *between 4 and 300 K. The χ vs.* T *curve exhibits two peaks: a large one at 15 K and a small one at 106 K. The magnetic susceptibility between the Néel temperature* $T_N = 106$ *K and 300 K obeys the predictions of the Stewart theory. We also demonstrate hysteretic effects in the magnetic susceptibility around* T_N *and indicate that no significant results on critical indices could be obtained from these measurements.*

1. INTRODUCTION

It is well known that the paramagnetic behavior of most rare earth metals can be satisfactorily explained[1] using the tripositive ion model and the Van Vleck theory of paramagnetism.[2] One rare earth metal whose paramagnetic properties deviates considerably from the predictions of the above model is samarium.[3] Recently Stewart[4] has developed a theory of metallic samarium which takes into account the influence of conduction-electron polarization effects and interionic Heisenberg exchange couplings. The lowest energy multiplet of Sm^{3+}, resulting from five localized f electrons, consists of six energy levels, $^6H_{5/2}$ being the ground state. According to Stewart, if one assumes that only the $^6H_{7/2}$ level is thermally populated as the temperature increases and if one neglects crystalline field effects, then the magnetic susceptibility can be written as

$$\chi = \chi_0 + C/(T - \theta) \tag{1}$$

where χ_0, C, and θ are constants. Equation (1) is a modified Curie–Weiss law which describes many paramagnetic systems possessing localized

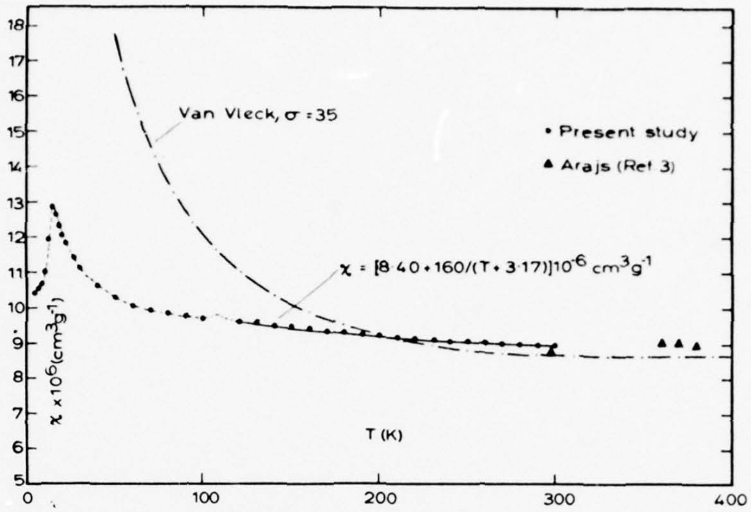


Fig. 1. Mass magnetic susceptibility of polycrystalline samarium between 4 and 400 K.

magnetic moments and conduction electrons. Stewart[4,6] examined the magnetic susceptibility data obtained by Jayaraman and Sherwood[5] using a rhombohedral samarium sample. He finds that Eq. (1), in the form of $\chi = [7.853 + 98.96/(T + 6.70)] \times 10^{-6}\ \mathrm{cm}^3/\mathrm{g}$, fits the experimental points to an accuracy of 0.5% between 15 and 100 K. We have two comments on this matter. First, the experimental points scatter considerably, as can be seen from Fig. 1 in Ref. 4. Second, rhombohedral samarium is magnetically ordered below 106 K (which Stewart rightly recognizes in Ref. 6) and thus the fit given above may not be particularly meaningful below 106 K. For these reasons we decided to obtain new magnetic susceptibility data on polycrystalline rhombohedral samarium between 4 and 300 K and to analyze them from existing theoretical viewpoints. The results of our studies are briefly described in this paper.

2. EXPERIMENTAL CONSIDERATIONS

Distilled samarium used in this investigation was purchased from Research Chemicals (Phoenix, Arizona). Before usage, it was arc-melted using the facilities and techniques described elsewhere.[7] The polycrystalline sample whose magnetic properties were studied was in the rhombohedral state. The magnetic susceptibility was measured using the equipment briefly described before.[8]

3. RESULTS AND DISCUSSION

Metallic rhombohedral samarium undergoes two magnetic transitions: one at about 15 K and another at about 106 K. According to neutron diffraction studies,[9] the lower temperature transition is associated with ordering of the magnetic moments on the cubic sites. The higher transition is due to ordering on the hexagonal sites. Above 106 K, which is the Néel temperature of samarium, this metal is in its paramagnetic state. The magnetic susceptibility measured with increasing temperatures, as can be seen from Fig. 1, exhibits anomalies at the transition temperatures mentioned above. There is a large peak at 15 K and much smaller one near 106 K. Since the behavior of χ in the neighborhood of 106 K is presented separately later in this paper, it is shown only schematically in Fig. 1.

The curve given in Fig. 1 was obtained by measuring the susceptibility in different applied magnetic fields and extrapolating the data to infinite-field values. The triangular points also shown in Fig. 1 are the susceptibility values obtained in an earlier high temperature study[3] using a different samarium sample and a different experimental facility. The agreement between the measurements is satisfactory.

The curve labeled "Van Vleck, $\sigma = 35$" in Fig. 1 represents the paramagnetic behavior of Sm^{3+} ions calculated from the Van Vleck susceptibility equation [Eq. (5) in Ref. 3]. The quantity σ is the nuclear screening constant. The energy levels associated with various values of σ have been calculated before (Table I in Ref. 3). The set of six energy levels associated with $\sigma = 35$ gives a reasonably good fit, without any adjustable constants, between 220 and 400 K. However, as can be seen from Fig. 1, the theoretical curve based on this model predicts much higher susceptibility values than those observed experimentally at lower temperatures. Thus Van Vleck theory mentioned above is not a satisfactory model of the magnetic susceptibility of samarium at low temperatures.

The solid curve through the experimental points between 120 and 300 K represents the equation

$$\chi = [8.40 + 160/(T + 3.17)] \times 10^{-6}\ \mathrm{cm}^3/\mathrm{g} \qquad (2)$$

This equation is of the form derived by Stewart, as mentioned above. Thus our paramagnetic data below 300 K are in good agreement with Stewart's theory. We note that the numerical constants in Eq. (2) are different from those obtained by Stewart in his analysis of the experimental data by Jayaraman and Sherwood. Very likely the purity of the samples is responsible for these differences. A recent study of the magnetic susceptibility of polycrystalline samarium by Perakis and Kern[10] clearly indicates that heat treatments can also strongly influence susceptibility values. It would be interesting to analyze these data from the viewpoint of the Stewart theory. However, this is not possible from a graphical representation of the data given in Ref. 10. It may be mentioned that their susceptibility measurements before heat treatments are in good agreement with our values in the corresponding temperature interval.

Figure 2 shows the magnetic susceptibility (in arbitrary units) in the neighborhood of the Néel temperature. Originally we expected to study the critical behavior of the susceptibility at this phase transition. However, Fig. 2 reveals two observations. First, the magnetic susceptibility of this particular sample depends on its thermal history. The warming run was made with increasing temperatures starting at 80 K. The run ended at 130 K. After reaching this point, the susceptibility was measured with decreasing temperatures down to 80 K. Second, the nature of the peak at 106 K is

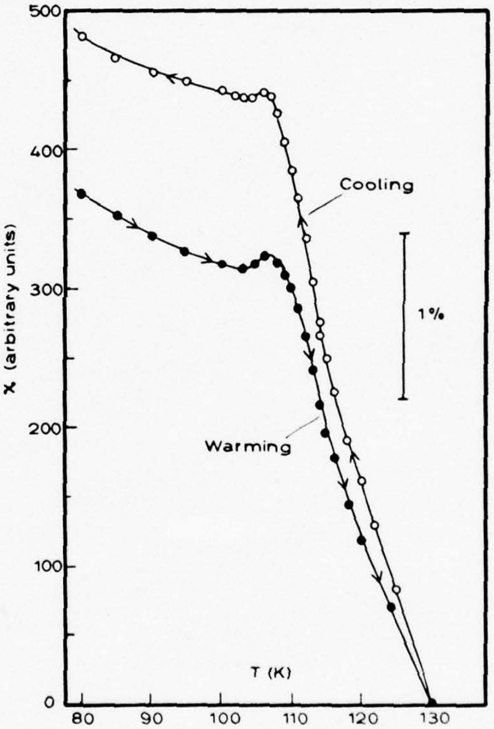


Fig. 2. Magnetic susceptibility of samarium in the neighborhood of the Néel temperature. These measurements we carried out in an external field of 7 kOe.

also influenced by the thermal treatment in this region. Thus it was decided that no significant results on critical indices could be obtained from these measurements.

Phenomenologically, we have found that the magnetic susceptibility of samarium below the peak occurring at $T_{\max} = 15$ K can be represented by the equation

$$\chi = A(T - T_{\max})^{-0.031} \tag{3}$$

where A is a constant. The above exponent correctly describes the susceptibility behavior for values of $T - T_{\max}$ up to 7 K.

In summary, we conclude that the Stewart theory appears to be applicable to paramagnetic samarium between 120 and 300 K. At the present time there is no satisfactory theory for the antiferromagnetic behavior of the two magnetic phases of samarium below the Néel temperature. Furthermore, the critical behavior of the magnetic susceptibility at the phase transitions described above is still in open question.

NOTE ADDED IN PROOF

After the completion of this paper, detailed investigations of the magnetic susceptibility on single Sm crystals were published by K. A. McEwen, P. F. Touborg, G. J. Cock, and L. W. Roeland [*J. Phys. F: Metal Phys.* **4**, 2264 (1974)]. This latter work clearly shows a large anisotropy in the magnetic susceptibility between the basal plane and the *c* axis, especially in the neighborhood of the magnetic transitions.

ACKNOWLEDGMENTS

We appreciate the technical help of Lutfi Klaif in making some of these measurements. The authors are grateful to the Office of Naval Research, U.S., and the Statens Naturvetenskapliga Forskningsrad, Sweden, for grants which made this study possible.

REFERENCES

1. S. Arajs and R. V. Colvin, "Paramagnetism of Polycrystalline Rare Earth Metals," in *Rare Earth Research*, E. V. Kleber, ed. (Macmillan, New York, 1961), p. 178.
2. J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).
3. S. Arajs, *Phys. Rev.* **120**, 756 (1960).
4. A. M. Stewart, *Phys. Rev. B* **6**, 1985 (1960).
5. A. Jayaraman and R. C. Sherwood, *Phys. Rev.* **134**, A691 (1964).
6. A. M. Stewart, *Phys. Rev. B* **8**, 2214 (1973).
7. S. Arajs and G. P. Wray, *J. Phys. E* **2**, 518 (1969).
8. L. Hedman, K. Svensson, K. V. Rao, and S. Arajs, *Phys. Lett.* **45A**, 175 (1973).
9. W. C. Koehler and R. M. Moon, *Phys. Rev. Lett.* **29**, 1468 (1972).
10. N. Perakis and F. Kern, *Compt. Rend.* **275**, 677 (1972).

12

Journal of Low Temperature Physics, Vol. 21, Nos. 3/4, 1975

Electrical Resistivity of Nickel-Rich Nickel–Chromium Alloys Between 4 and 300 K

Y. D. Yao, Sigurds Arajs, and E. E. Anderson

Department of Physics, Clarkson College of Technology, Potsdam, New York

(Received April 18, 1975)

Electrical resistivity ρ of Ni–Cr alloys containing 5.5, 11.3, 15.7, 16.8, 19.4, 22.0, 24.6, and 27.0 at % Cr has been measured as a function of the absolute temperature T *between 4 and 300 K. The sample with the Cr content of 22.0 at % exhibits a small ρ minimum at about 10 K. No minimum has been observed in any other of the above samples, although an anomalous* T *dependence has been found in alloys containing 15.7, 16.8, and 19.4 at % Cr. The ρ minimum has been discussed from the viewpoint of the Béal-Monod theory for the Kondo effect in concentrated systems and the mechanism by Greig and Rowlands based on a* T*-dependent decrease of the impurity electrical resistivity. It is concluded that the ρ minimum in the Ni–Cr system is still a phenomenon which is not well understood at the present time.*

1. INTRODUCTION

Pandorf, Lerner, and Daunt[1,2] in 1964 and Hust[3] in 1972 measured the electrical resistivity ρ of Evanohm wire (Ni 75 wt %, Cr 20 wt %, Al 2.5 wt %, Cu 2.5 wt %) below room temperature. Their results strongly suggest the existence of a minimum in the ρ curve somewhere between 4 and 20 K. It is reasonable to assume that the role of Al and Cu is not important for the formation of this minimum. Thus the above studies imply that the electrical resistivity of Ni–Cr alloys at low temperatures also could behave anomalously. No studies from this viewpoint of the electrical transport properties on this system have been done before. Therefore, we decided to measure the electrical resistivity of Ni-rich Ni–Cr alloys containing different concentrations of Cr between 4 and 300 K. Our results and their significance are presented in this paper.

2. EXPERIMENTAL DETAILS

The Ni–Cr alloys containing 5.5, 11.3, 15.7, 16.8, 19.4, 22.0, 24.6, and 27.0 at % Cr were prepared by an electric arc melter.[4] The stock of Ni was purchased from Johnson, Mathey and Co. The analysis of the impurities found in this material has been given previously.[5] The Cr was obtained from Chromalloy Corporation. Its purity has also been reported elsewhere.[6] After repeated melting (two or three times), the ingots, weighing about 20–30 g, were sealed into silica tubes under 1/5 atm pressure of Ar at room temperature and homogenized at 1000°C for six days. The silica capsules were rapidly quenched in ice water. From these ingots samples in the form of rectangular parallelepipeds were cut by hand using a diamond saw. The surfaces of these samples were polished using files and sandpaper. Typical sample dimensions were roughly $3 \times 3 \times 30\,\mathrm{mm}^3$.

The ρ of the above samples was determined using the conventional four-probe technique. Two Cu wires, lightly spot-welded to the broad face of each sample, were used as the potential contacts. The two current leads (using Cu wire) were soldered near each end of the sample. The data of ρ as a function of the absolute temperature T were obtained using the methods and the equipment described before.[7] The ρ values reported in this paper have not been corrected for the thermal expansion effects. The maximum relative error at liquid He temperatures arising from the neglect of this correction would be about 0.3 %. It is estimated that any error in ρ resulting from the form factor measurements at room temperature is not larger than 1 %. The errors in the temperature measurements have been discussed elsewhere.[7]

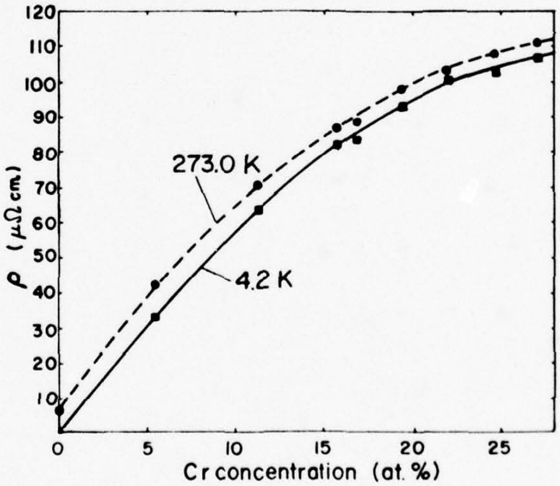


Fig. 1. Electrical resistivity of Ni–Cr alloys as a function of chromium concentration at 4.2 and 273.0 K.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the values of ρ of our Ni–Cr alloys as a function of Cr content at 4.2 and 273 K. These plots confirm the expected good quality of the alloys prepared by the methods described above. The residual resistivities of the Ni–Cr system with Cr content up to about 5 at % have been studied before by Schwerer and Conroy.[8] Their data appear to be in good agreement with our results. Our values at 273 K are in good agreement with those due to Köster and Gmöhling[9] measured at room temperature.

Figure 2 presents the ρ vs. T curves between 4 and 300 K. Two facts are evident from these plots. First, Cr drastically increases ρ of Ni. Second, the temperature coefficient of ρ is very small, especially for the alloy containing 22.0 at % Cr. Details of the ρ behavior between 4 and 50 K are

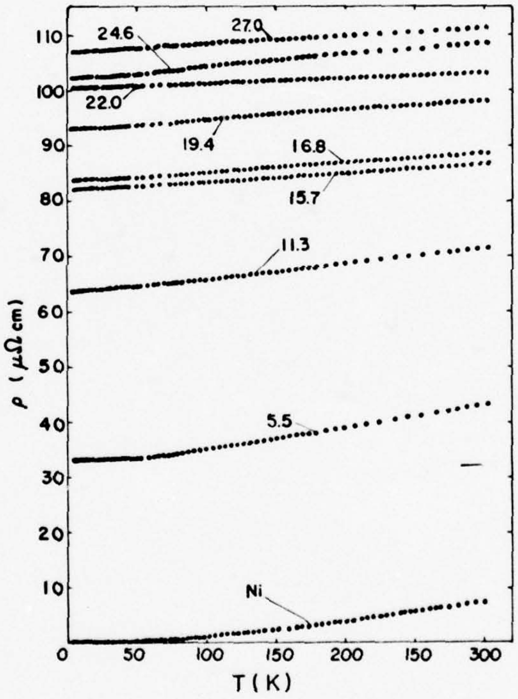


Fig. 2. Electrical resistivity of Ni–Cr alloys as a function of temperature between 4 and 300 K. The numbers indicate the atomic percentages of Cr.

shown in Fig. 3. It is obvious that the alloys containing 15.7, 16.8, 19.4, and 22.0 at % Cr clearly exhibit an anomalous behavior in this temperature range. The alloy having 22.0 at % Cr concentration (which corresponds to the 20 wt % Cr content in Evanohm metal) shows a small ρ minimum (of the depth of about 0.05 $\mu\Omega$-cm) at about 10 K. No such minimum has been observed in any other Ni–Cr alloy used in this study. The nature of this minimum is shown even more clearly in Fig. 4. Thus our results confirm the suggestion that the expected minimum in Evanohm is due to Ni and Cr and not because of small additions of Al and Cu. It appears that the existence of such a minimum is likely restricted to a very narrow composition range of Cr because it is absent (at least above 4.2 K) in the alloys containing 19.4 and 24.6 at % Cr. It should be remarked that this minimum behavior in the 22.0 at % Cr sample has been obtained from three different temperature runs.

A very small minimum in the electrical resistivity at about 2.8 K has been seen recently[10] in an atomically disordered Ni–Pt alloy containing 50 at % Pt. This alloy is in a weakly ferromagnetic state at liquid He temperatures. The strange anomalous behavior originated a development of a

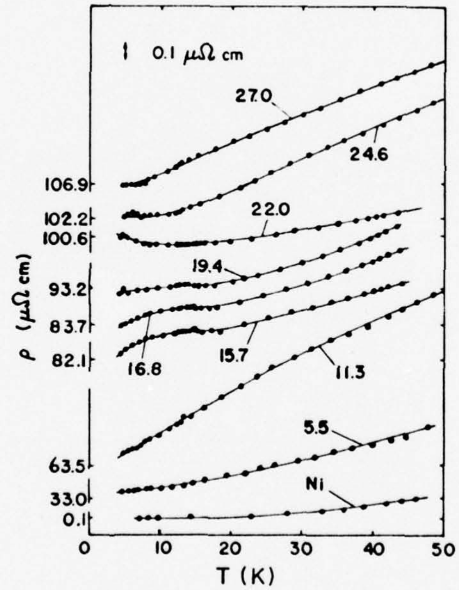


Fig. 3. Electrical resistivity of Ni–Cr alloys as a function of temperature between 4 and 50 K. The numbers indicate the atomic percentages of Cr.

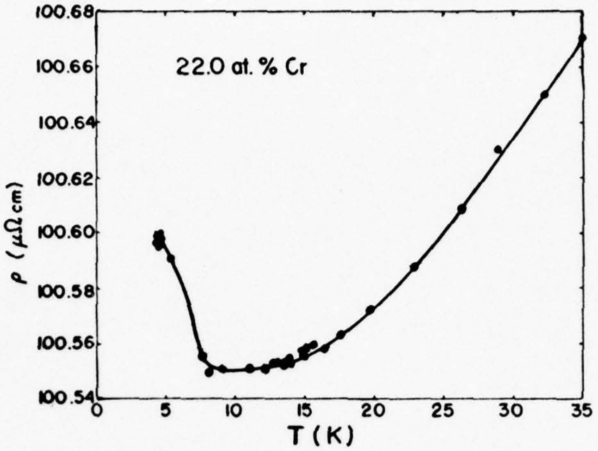


Fig. 4. The electrical resistivity minimum of the Ni–Cr alloy containing 22.0 at % Cr.

theoretical model by Béal-Monod[11] for the electrical resistivity in concentrated atomically disordered ferromagnetic alloys satisfying special conditions. She was able to derive a Kondo-type (logarithmic in T) contribution $\rho_{T\to T_C}$ to the total electrical resistivity slightly below the ferromagnetic Curie temperature T_C, using the second Born approximation. Essentially, she recognized the analogy between the electrical magnetoresistivity of dilute Kondo alloys[12] and the resistivity of ferromagnetic metals[13] near T_C. Thus, she obtained in the ferromagnetic region

$$\rho_{T\to T_C} \propto \left(J^2 + \frac{3J^3 z}{E_F} \ln \frac{kT}{2E_F}\right)\left[s(s+1) - \lambda\left(\frac{\gamma\sigma}{kT}\right)^2\right] \tag{1}$$

where J is the exchange interaction constant, s is the impurity spin, E_F is the Fermi energy, z is the number of electrons per atom, k is the Boltzmann constant, γ is the molecular field constant $[\gamma = 3kT_C/s(s+1)]$, σ is the spontaneous magnetization, and

$$\lambda \approx \tfrac{1}{3}s(s+1)[\tfrac{1}{3}s(s+1) + (4/9)] \tag{2}$$

for $T \sim T_C$. Equation (1) implies that there is a resistivity minimum if $J < 0$ and if the following other conditions are satisfied: (1) temperatures are close to T_C, (2) T_C is small so that the minimum is not destroyed by phonons, (3) σ does not vary much with T near T_C and (4) $\gamma\sigma \leq kT$. Béal-Monod also suggests that in the paramagnetic region, due to the short-range spin ordering by local molecular field, a weak Kondo-like behavior may be expected. However, if paramagnons (strong enhanced spin fluctuations) are present, these will dominate the ρ behavior (proportional to T^2) and will overcome the small negative $\ln T$ term due to the local ordering. Furthermore, Béal-Monod strongly suspected that the resistivity minimum observed in the 50 at % Ni–50 at % Pt sample was due to the mechanism described above. At first glance, it is tempting to think that the minimum in the ρ vs. T curve of the Ni–Cr alloy containing 22.0 at % Cr is also due to the same cause. However, there are some difficulties with this idea. The ρ minimum mentioned above in the Ni–Pt system was found only when the alloy was in an atomically disordered, weakly ferromagnetic state. The minimum disappeared when this alloy was atomically ordered by thermal annealing, which converted it to a paramagnetic system. However, our Ni–Cr alloy, exhibiting the ρ minimum, was in a paramagnetic state at liquid He temperatures. This we conclude from the Curie point determinations by Sadron,[14] Marian,[15] and Besmus *et al.*[16] Their results are presented in Fig. 5. From this plot one can see that the older studies by Sadron and Marian give considerably higher values of T_C than given by Besmus *et al.*, whose determinations have been recently confirmed by Gregory and Moody.[17] The latter data are not plotted in Fig. 5 because these investigators do not give numerical values of T_C in their paper. Figure 5 clearly implies that the ferromagnetic state in the Ni–Cr system disappears at about 13

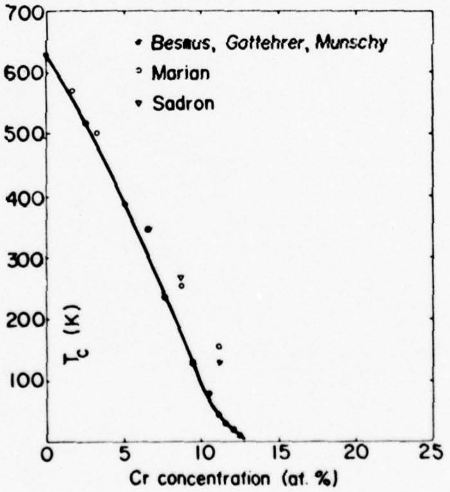


Fig. 5. Ferromagnetic Curie temperatures of Ni–Cr alloys.

at % Cr concentration. This expectation is also consistent with the magnetization studies[16,18] and the electronic specific heat measurements.[17] It was mentioned above that according to Béal-Monod the ρ minimum can also be present in a paramagnetic alloy if paramagnons are absent. Thus, if we assume that there are no strong enhanced spin fluctuations in the Ni–Cr system near the critical composition for ferromagnetic ordering, then there could be a ρ minimum in our 22.0 at % Cr sample even if it is in a paramagnetic state. Unfortunately, the absence of paramagnons in the Ni–Cr system may not be realistic because such excitations have been observed in numerous other systems based on transition metal alloys. We have examined the T dependence of the ideal electrical resistivity of the alloys containing 19.4, 22.0, 24.6, and 27.0 at % Cr. In general, the T dependence is complicated, especially in the alloys exhibiting anomalous low T behaviour (Fig. 3). None of the above alloys shows T^2 dependence expected for the conventional electron–paramagnon scattering.[19]

Finally, it should be mentioned that recently very small minima in the ρ vs. T curves have been observed by Greig and Rowlands[20] in some Pd alloys containing Rh, Ru, and Pt. They conclude that these minima are not due to the Kondo scattering. In fact, they convincingly suggest that the minima result from a temperature-dependent decrease of the impurity resistivity attributed to a reduction in the s–d scattering with increasing temperatures. To a first approximation, this interband mechanism modifies the residual resistivity by a factor $(1 - AT^2)$, where

$$A = \frac{\pi^2 k^2}{6} \left\{ 3\left[\frac{1}{N_d(E)} \frac{dN_d(E)}{dE} \right]^2 - \frac{1}{N_d(E)} \frac{d^2 N_d(E)}{dE^2} \right\}_{E=E_F} \tag{3}$$

where E is the energy and $N_d(E)$ is the electronic density of states of d electrons. According to this prediction, based on the rigid band model approximation, the increase in ρ below the minimum should vary as T^2. Our 22.0 at % Cr in Ni alloy does not exhibit such a T dependence. In fact, the increase, within the experimental error, is quite proportional to ln T. Since detailed information on the density of states in the d band for Ni–Cr alloys is not available for numerical calculations of this type, it is difficult to pursue this problem further. It should be remarked that recently the electronic structure of Ni base for ferromagnetic alloys has been studied by Hasegawa and Kanamori[21] using the coherent potential approximation based on a tight-binding single-band model. They predict that the spin-up band splits into two subbands. The band above the Fermi level corresponds to Friedel's virtual bound state in his single-impurity theory.[22] In the case of the Ni–Cr system the virtual bound state is just above the Fermi level, overlapping the majority spin band. This overlap gives rise to the high electrical resistivity of Ni–Cr alloys shown in Fig. 2. According to Hasegawa and Kanamori, the ferromagnetism of the Ni–Cr system gradually transforms to a split band paramagnetism at 11 at % Cr concentration. It is possible that the unique electronic structure of Ni–Cr alloys is somehow responsible for the ρ minimum described above. From this viewpoint, it would be of interest to examine in detail the behavior of ρ of Ni–Mn alloys, which possess somewhat similar electronic structure. Unfortunately, none of the above theoretical approaches sheds any light on the anomalous ρ behavior seen in the Ni alloys containing 15.7, 16.8, and 19.4 at % Cr. In summary, it appears that the origin of the anomalous behavior in ρ at low T of Ni–Cr alloys described in this paper is not well understood at the present time.

ACKNOWLEDGMENTS

The authors are grateful to the Office of Naval Research for their financial support of this work under Grant N00014-70-A-0311. Stimulating discussions with Prof. K. V. Rao are greatly appreciated.

REFERENCES

1. E. Lerner and J. G. Daunt, *Rev. Sci. Instr.* **35**, 1069 (1964).
2. R. C. Pandorf, E. Lerner, and J. G. Daunt, *Rev. Sci. Instr.* **35**, 1070 (1964).
3. J. G. Hust, *Rev. Sci. Instr.* **43**, 1387 (1972).
4. *S. Arajs and G. P. Wray, J. Phys. E.* **2**, *518 (1969).*
5. S. Arajs, H. Chessin, and R. V. Colvin, *Phys. Stat. Sol.* **3**, 2337(1963).
6. S. Arajs and G. R. Dununyre, *J. Appl. Phys.* **36**, 3555 (1965).
7. S. Arajs, *Can. J. Phys.* **47**, 1005 (1969).
8. F. C. Schwerer and J. W. Conroy, *J. Phys. F* **1**, 877 (1971).
9. W. Köster and W. Gmöhling, *Z. Metalkunde* **52**, 713 (1961).
10. A. I. Schindler and D. J. Gillespie, in *Proc. 12th Int. Conf. Low Temperature Physics, Kyoto, 1972*, E. Kanda, ed. (Academic Press of Japan, Kyoto, 1971), p. 777.
11. M. T. Béal-Monod, *Solid State Comm.* **9**, 401 (1971).
12. M. T. Béal-Monod and R. A. Weiner, *Phys. Rev.* **170**, 552 (1968).
13. T. van Peski-Tinberger and A. J. Dekker, *Physica* **29**, 917 (1963).
14. C. Sadron, *Ann. Phys.* (*Paris*), **17**, 371 (1932).
15. P. V. Marian, *Ann. Phys.* (*Paris*) **7**, 459 (1937).
16. M. J. Besmus, Y. Gottehrer, and G. Munschy, *Phys. Stat. Sol.* (*b*) **49**, 597 (1972).
17. I. P. Gregory and D. E. Moody, *J. Phys. F* **5**, 36 (1975).
18. R. Chiffey and T. J. Hicks, *Phys. Lett.* **34A**, 267 (1971).
19. A. I. Schindler and M. J. Rice, *Phys. Rev.* **164**, 759 (1967).
20. D. Greig and J. A. Rowlands, *J. Phys. F* **4**, 536 (1974).
21. H. Hasegawa and J. Kanamori, *J. Phys. Soc. Japan* **33**, 1599 (1972).
22. J. Friedel, *Nuovo Cimento Suppl.* **7**, 287 (1958).

Proc. 14th International Conf. on Low Temperature Phys, Vol. 3 — Low Temperature Properties of Solids, edited by M. Krusius and M. Vuorio (North-Holland Publishing Company, Amsterdam, 1975), p. 231–233

13

L.061 FIRST-ORDER MAGNETIC PHASE TRANSITION IN Cr-Si ALLOYS

S.Arajs and K.V.Rao, C.C.T., POTSDAM, N.Y., USA and
L.Hedman and H.U.Åström, KTH, STOCKHOLM, SWEDEN

First-order transitions in the Cr-Si system were discovered for the first time in 1967 using electrical resistivity (ρ) measurements.[1] Recently such transitions have also been confirmed from the viewpoint of magnetic susceptibility (χ)[2] and thermal expansion[3] studies. This type of transition is very rare in binary chromium systems. Besides Si only Fe is known to cause such a phenomenon. In order to increase our knowledge about the role of Si in Cr, we decided to obtain detailed χ data between 4.2 and 340K on Cr-Si alloys exhibiting the first-order transitions. This property has never been measured as a function of the absolute temperature (T) before. Our results are briefly described in this communication.

The Cr-Si alloys used in this study are the same whose ρ was studied before.[1] The χ values were measured using experimental facilities described elsewhere.[2]

Figure 1 shows χ as a function of T, of Cr and Cr alloys containing 1.37, 1.85, 2.74 and 3.19 at% Si, between 4.2 and 340K. The first-order transitions, taking place at the same T, where abrupt changes in ρ have been seen before, are clearly noticeable from this plot. The ρ of the sample with 1.37 at% Si shows a small minimum[1] at about 110K. This ρ anomaly has been recently confirmed in our laboratory[4]. The χ data, however, within the experimental error, do not show any irregularity in the neighbourhood of 110K. Thus the nature of this anomaly is still unclear at the present time. The hysteresis effects at the first-order transitions seen in the ρ vs T curves[1] are also noticeable (not shown in fig.1) in the χ studies.[2]

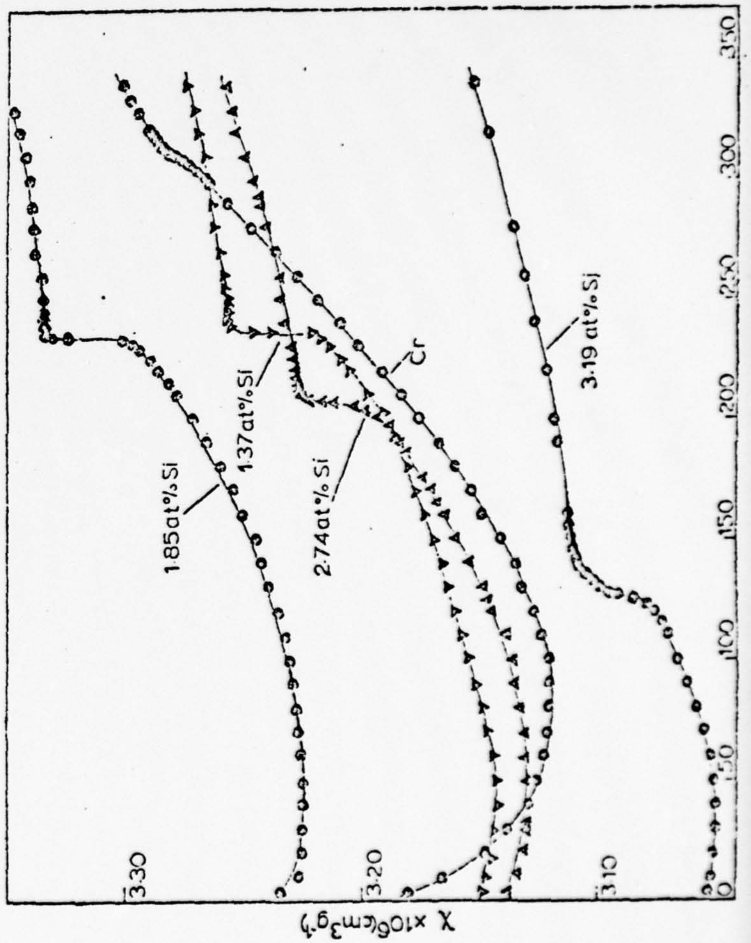
A few other interesting facts can be seen from the χ vs T curves of Cr-Si alloys. First, the χ values at any T in either the antiferromagnetic or paramagnetic region exhibit a complicated composition dependence possibly indicating a strong band structure effect. Second, additions of Si to Cr decrease the low T increase in the χ vs T curve of Cr. We feel that this again is a band structure effect and is not associated with any ferromagnetic contamination. Third, the behaviour of χ just above the first-order transition is remarkably independent of T for about 20K range in alloys containing 1.37 and 1.85 at% Si.

Our χ studies have clearly confirmed that there are first-order magnetic transitions in the Cr-Si system. The nature of these transitions is not completely clear at the present time. Neutron diffraction investigations are badly needed for further elucidation of the magnetic phase diagram of Cr-Si system. Further analysis of the χ vs T data of Cr-Si alloys from the viewpoint of the extended Fedders and Martin theory is in progress.[5]

The authors are grateful to ONR(USA) and NFR(SWEDEN) for their financial support. We thank Lutfi Klaif for his help in making some of these measurements.

References:

1. S.Arajs and Wm.E.Katzenmeyer, J.Phys.Soc.Japan 23, 932(1967)
2 L.Hedman, K.Svensson, K.V.Rao, and S.Arajs, Physics Letters 45A, 175 (1973)
3 K.Fukamichi and H.Saito, J. Phys.Soc.Japan 38, 287(1975)
4 D.Abukay, K.V.Rao and S.Arajs (unpublished results)
5 S.Arajs, C.A.Moyer, J.R.Kelly, and K.V.Rao (to be published)



14 – Low Temperature Properties of Solids, edited by M. Krusius and M. Vuorio (North-Holland Publishing Company, Amsterdam, 1975), p. 398-401

MAGNETIC SUSCEPTIBILITY OF Pd-Ce ALLOYS AT LOW TEMPERATURES

K.V.Rao, S.Arajs and Y.D.Yao, C.C.T., POTSDAM, N.Y., USA and
L. Hedman, Ch. Johannesson and H.U.Åström, KTH, STOCKHOLM, SWEDEN.

The possibility that Pd-Ce alloys might be a Kondo system in the presence of crystalline fields has been of interest to experimentalists.[1-5] Magnetic susceptibility (χ) studies by Shaltiel et al[1] on Pd+4 at% Ce implies that there is a magnetic moment of 1.1 μ_B on Ce atoms, which is lower than the free ion value of 2.5 μ_B. However, Guertin et al[2] find it $<10^{-3} \mu_B$ per Ce atom, suggesting a Ce^{4+} valence state. Similar conclusions have been reached by Harris et al[3] and Speight[4]. Recently Mydosh[5] found a weak resistivity (ρ) minimum (a few parts in 10^4) below 10K, but indirectly concluded that Ce impurities are in the non-magnetic Ce^{4+} valence state. Because of the limited nature of the χ studies mentioned above and some inconsistencies in the results we decided to investigate further the role of Ce in Pd. Here we discuss briefly our χ and ρ studies on 0.4, 0.9 & 1.4 at% Ce in Pd.

The alloy melts were prepared by arc melting using Ce from Research Chemicals and Pd from Engelhard Industries. After melting, the ingots were sealed in silica tubes under 1/5 atm pressure of Ar at room temperatures and were annealed at 1000C for 6 days.

The χ behaviour of our Pd-Ce alloys in the range 1.5-340K is shown in Fig. 1. Clearly, additions of Ce considerably lower the χ values of Pd above 10K. In principle, this is consistent with the studies at 17C by Harris et al[3]. Our χ results support the previous conclusions that Ce enters a Pd matrix essentially as a non-magnetic 4+ ion at least above 20K. The large initial decrease in χ due to Ce additions strongly suggests some electron transfer processes and a change in the electronic band structure in Pd. It is also evident that Ce depresses the size of the characteristic χ maximum of Pd at 80K on alloying. Below 10K χ increases rapidly with decreasing temperatures. Such an increase is also observed in pure Pd used to make these alloys. Additions of Ce to Pd cause an anomalous behaviour in the χ vs Ce conc. curve at low T as seen from the insert in Fig. 1. For a detailed analysis we have also studied the χ dependence on applied magnetic fields.

We find that χ of Pd and Pd-Ce alloys can be described by the equation $\chi = A + C/(T-\theta)$, where A,C and θ are constants and T is the absolute temperature. The values of these constants are given in Table I. If we assume that the value of effective magnetic moment of Fe in Pd is $10\mu_B$, then the value of C obtained for Pd gives the conc. of Fe to be 30ppm. This result is in excellent agreement with our analytical determination on the initial stock of Pd used to make these alloys. Furthermore, if we assume that there are no localized moments on Ce ions then the values of C in Table I give the magnetic moment on Fe to be 17.6,17.3 and $15.4\mu_B$ for 0.5,0.9 and 1.4 at% Ce samples, respectively. If it is assumed that the moment of Fe is $10\mu_B$ and remains unchanged when Ce is added to Pd, the values of C imply a magnetic moment on Ce atoms of 1.3,1.0 and $0.7\mu_B$, respectively. Although it is impossible to strongly favour either of these possibilities, an increased average moment on Fe atoms might be a result from clustering effects stimulated by the presence of Ce ions. Harris et al[3] have noticed that Ce drastically reduced the solubility of Fe in Pd. Further support to this point of view is seen from our electrical resistivity data on these alloys (fig.2) below 50K. We do not see any minimum, but samples containing 0.5 and 1.4 at% Ce show spectacular anomalies at low temperatures. Such a behaviour however, is absent in the sample with 0.9 at% Ce. Clustering of Fe atoms mentioned above is probably the source of these anomalies. It would be very interesting to explore further the role of Ce on the giant moments of Fe in Pd under preselected conditions.

The authors are grateful to NSF(USA) and NFR(Sweden) for their financial support.

REFERENCES:

1 S.Shaltiel, J.H.Wernick, H.J.Williams and M.Peter, Phys. Rev. A1 35, 1346 (1964)

2 R.P.Guertin, H.C.Pradduade, S.Foner, E.J.McNiff Jr, and B.Barsonmian, Phys. Rev. B7, 274 (1973)

3 I.R.Harris and M. Norman, J.Less-Common Metals 15,285(1968)

4 J.D.Speight, J. Less-Common Metals, 30, 159(1973)

5 J.A.Mydosh in Low Temp. Phys-LT13(1973) (Plenum Publishing Corpn. New York 1974) ed. K.D.Timmerhaus, W.J.O'sullivan and E.F. Hammel, p. 506.

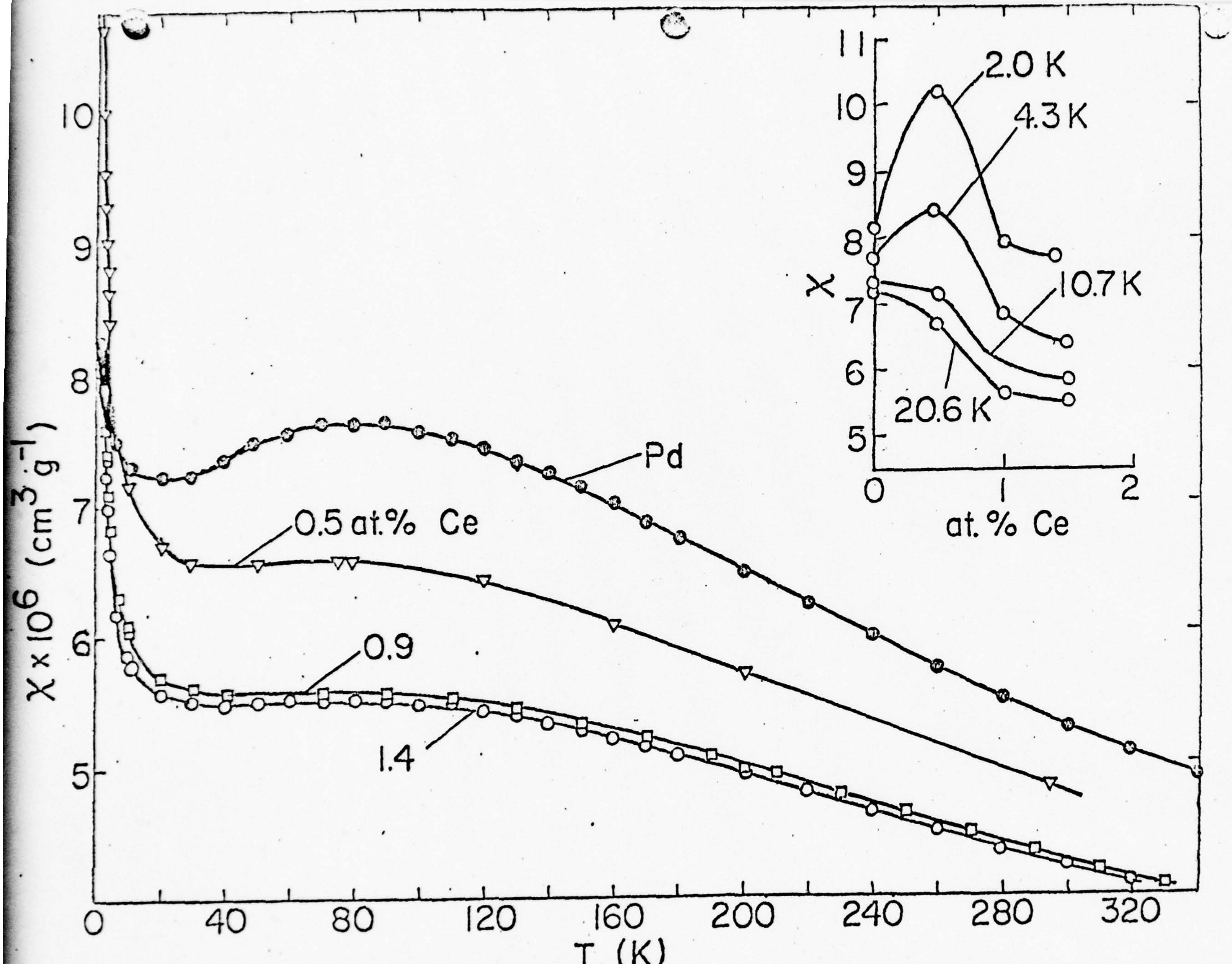


Fig.1 Magnetic Susceptibility of Pd-Ce Alloys.

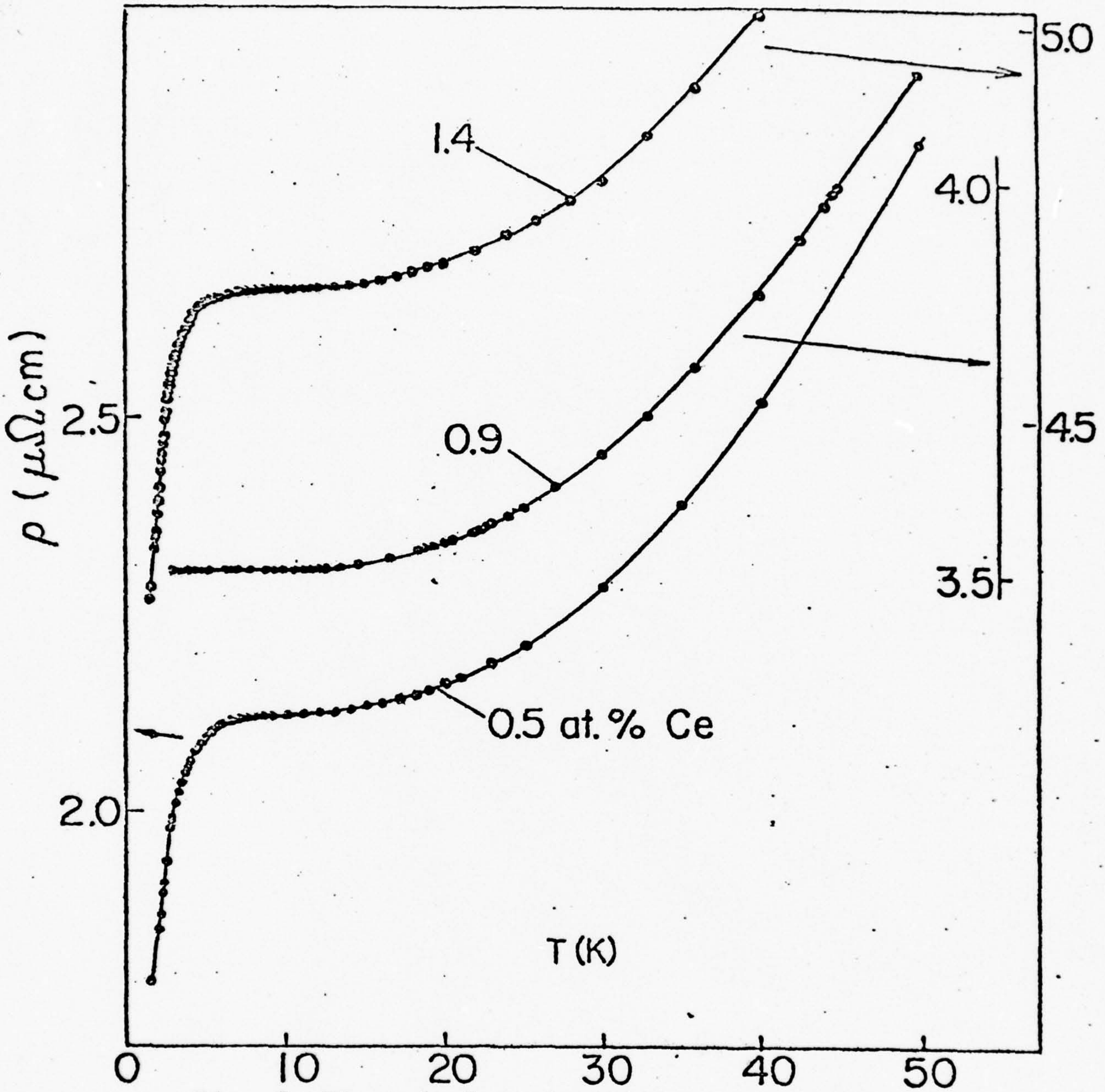


Fig. 2 Electrical Resistivity of Pd-Ce alloys.

Table I: $\chi = A + C/(T-\theta)$ fit of susceptibility data.

Ce Conc.(at%)	A($\times 10^6 cm^3 g^{-1}$)	θ (K)	C($\times 10^6 cm^3 g^{-1}$)
0	7.06	-1.2	3.55
0.5	6.09	-0.9	10.87
0.9	5.40	-2.3	10.53
1.4	5.18	-1.3	8.30

15

PHYSICAL REVIEW B VOLUME 12, NUMBER 7 1 OCTOBER 1975

Magnetic susceptibility of chromium-ruthenium alloys between 300 and 600 K

Sigurds Arajs, C. A. Moyer, J. R. Kelly, and K. V. Rao
Department of Physics, Clarkson College of Technology, Potsdam, New York 13676
(Received 5 May 1975)

Magnetic susceptibility χ of chromium-ruthenium alloys containing 0.9-, 2.1-, 3.0-, 4.8-, 6.6-, 8.3-, and 10.1-at.% ruthenium has been measured as a function of temperature T between 300 and 600 K. Each of the χ vs T curves exhibits a well-defined knee at the Néel temperature T_N. Experimental results indicate that there is no localized magnetic moment on ruthenium atoms above T_N. The temperature dependence in the antiferromagnetic region between 350 K and T_N is described by extending the Fedders-Martin theory for itinerant-electron antiferromagnets.

INTRODUCTION

Investigations[1,2] of the electrical resistivity ρ of binary chromium alloys containing ruthenium up to 14 at.% have clearly revealed very large anomalies in the neighborhood of their Néel temperatures T_N. In fact, the increases in the electrical resistivity below T_N are the largest ever observed in any binary chromium alloys except certain chromium-iron solid solutions.[3] At the present time there are no quantitative theories for such a behavior of the electrical transport properties in the neighborhood of T_N of chromium alloys. According to the above studies, T_N of chromium-ruthenium alloys increases rapidly with increasing ruthenium concentration reaching a maximum of about 555 K at the 3.5-at.% level. Addition of ruthenium above this concentration gradually decrease the values of T_N back to room temperatures.

The magnetic susceptibility χ of binary chromium alloys has not been studied extensively before. The only previous work on the chromium-ruthenium system from this viewpoint is that due to Booth,[4] and Bender and Müller.[5] Booth reports in a short letter the effects of ruthenium concentration on T_N of chromium which are in good agreement with the findings of the electrical studies mentioned above. Because chromium possesses such a unique antiferromagnetic structure, it seems that careful magnetic susceptibility studies of binary chromium alloys would be of considerable interest for further understanding of the itinerant-electron antiferromagnetism. Recently we have initiated such studies on numerous binary chromium systems. Our results on the chromium-cobalt system, where localized moments exist on cobalt atoms, has been briefly reported before.[6] In this paper, we present the magnetic-susceptibility studies on chromium-ruthenium alloys and discuss their significance.

EXPERIMENTAL CONSIDERATIONS

All the alloys used in this investigation are the same as those used in the previous electrical-resistivity studies.[1,2] The susceptibility samples having dimensions approximately 3×3×15 mm were cut from the arc-melted ingots also used for the transport property work.

The susceptibilities were determined using the Faraday method. Force measurements were made with an Ainsworth type 15 electrobalance. The signal output from the balance was read on a Hewlett-Packard 3439 digital voltmeter coupled to a Hewlett-Packard 3443-A range unit. The sensitivity of this system was 10 μg.

Samples were suspended in the magnetic field ($H dH/dz \approx 4\times 10^6$ Oe^2 cm^{-1}) in a quartz bucket which was connected to the balance by quartz-rod links. Temperatures between 300 and 650 K were produced by a bifilarly-wound (nickel chromalloy) furnace. The interior of the furnace could be evacuated and subsequently filled with gaseous argon. The temperatures were controlled to within ±0.01 K in the lower-temperature region and ± 0.1 K for temperatures above about 500 K. Temperatures were measured using Chromel-Alumel thermocouples. The temperature control was achieved by a modular M-Line Leeds and Northrup assembly.

RESULTS AND DISCUSSION

The mass magnetic susceptibility of chromium and chromium-ruthenium alloys containing 0.9-, 2.1-, 3.0-, 4.8-, 6.6-, 8.3-, and 10.1-at.% ruthenium is shown in Fig. 1. There is a small anomaly at T_N of pure chromium which has been recently studied in considerable detail.[7] As can be seen from Fig. 1, additions of ruthenium make this anomaly more pronounced at their respective T_N. The values of T_N can be obtained from Fig. 1 as temperatures at which the χ-vs-T curves exhibit a knee. These temperatures are listed in Table I and shown in Fig. 2 in comparison with the values of T_N determined from the previous electrical-resistivity studies.[2] The agreement between the two determinations is satisfactory.

Figure 1 shows that small amounts of ruthenium rapidly increase T_N of chromium reaching a maximum value of 555 K at about 3.5 at.% level. Larg-

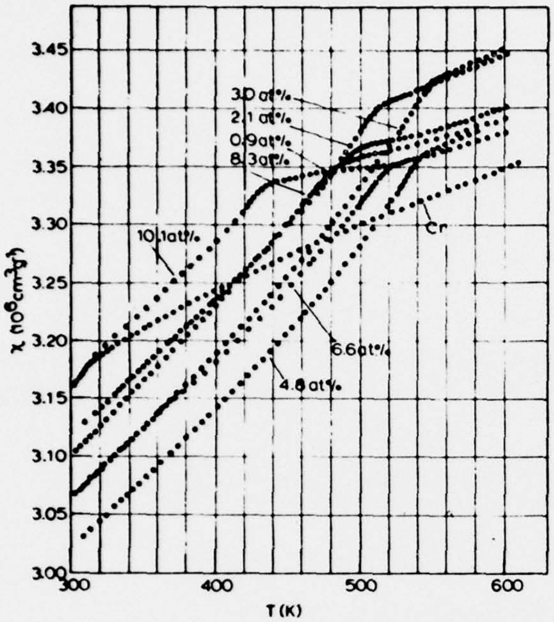


FIG. 1. Magnetic susceptibility of chromium-ruthenium alloys between 300 and 600 K. Only a representative set of data points are shown.

er ruthenium concentrations cause a gradual decrease in T_N. Speculations have been made that this behavior results from the crossover of the electron and hole Fermi surfaces[4] or from the delocalization effects of the d-electron wave functions.[8] However, it appears that, at the present time, there is no theory which could satisfactorily explain the above behavior.

The most conventional interpretation of magnetic-susceptibility data on dilute alloys is to assume that the total mass magnetic susceptibility of a particular alloy consists of two components, the susceptibility of the matrix χ_0 and the susceptibility of the solute impurity χ_{Ru}. Then

$$\chi = W\chi_{Ru} + (1 - w)\chi_0, \tag{1}$$

where w is the weight fraction of ruthenium in chromium. If it is assumed that the contribution χ_0 is independent of the solute concentration and equal to that of pure chromium, above T_N in all the alloys, then from Eq. (1) it is possible to calculate χ_{Ru}. This type of analysis has been recently applied by us to the chromium-cobalt system,[6] clearly indicating that a localized magnetic moment exists on cobalt atoms. Such an analysis gives χ_{Ru} independent of temperature for all ruthenium concentrations except 0.9 at.%. For this latter sample, χ_{Ru} decreases slightly with increasing temperature but does not follow a well-defined Curie-Weiss law. This strongly suggests that there is no localized magnetic moment on ruthenium atoms at least above T_N. Thus the magnetic properties of the above chromium-ruthenium alloys should be analyzed from the viewpoint of an itinerant-electron antiferromagnetism. Attempts to obtain a theory of such itinerant-electron antiferromagnets have been made by Zuckermann,[9] Fedders and Martin,[10] Maki and Sakurai,[11] and Crisan.[12]

TABLE I. Néel temperatures of chromium-ruthenium alloys.

Ru concentration (at.%)	T_N (K)
0.9	498
2.1	512
3.0	551
4.8	544
6.6	521
8.3	483
10.1	436

According to the two-band model of Fedders and Martin, the magnetic susceptibility (to the first order of their calculations) above T_N should be constant. Below T_N, the magnetic susceptibility is depressed because of the gap energy which keeps the spins antiferromagnetic. If one assumes a linearly polarized spin-density wave in y direction, then the parallel and perpendicular components of the magnetic susceptibility are

$$\chi_{\parallel} = \chi_{yy} \quad \text{and} \quad \chi_{\perp} = \chi_{xx} = \chi_{zz}\,, \tag{2}$$

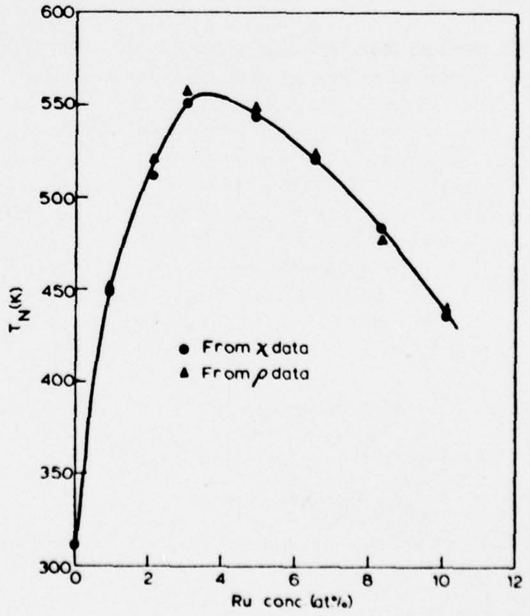


FIG. 2. Néel temperatures of chromium-ruthenium alloys.

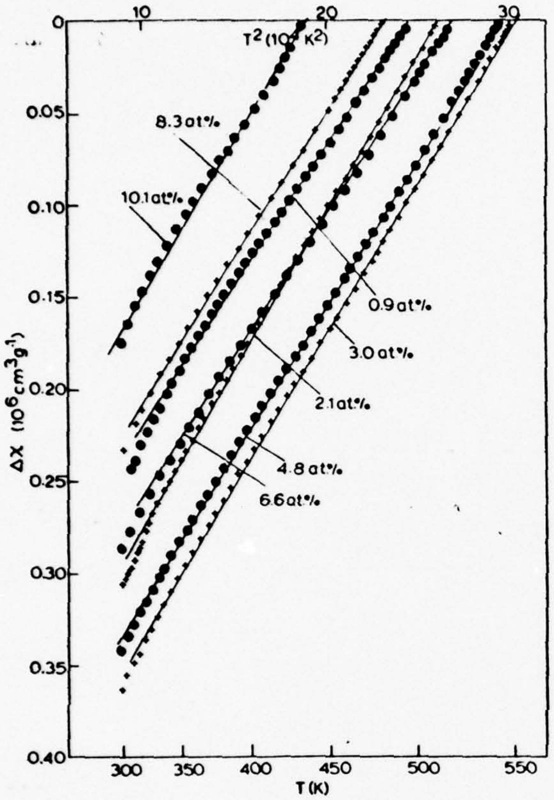


FIG. 3. Δχ as a function of T^2 for chromium-ruthenium alloys.

such that the total susceptibility for a polycrystalline material is

$$\chi = \tfrac{1}{3}\chi_{\parallel} + \tfrac{2}{3}\chi_{\perp}\,. \tag{3}$$

Fedders and Martin find that just below T_N, i.e., for $T_N - T \ll T < T_N$,

$$\chi_{zz} = \chi_{xx} = \chi_{zz}(T_N)[1 - 2(1 - T/T_N)]. \tag{4}$$

Since the anisotropy vanishes at the transition temperature, $\chi_{yy} = \chi_{zz}$ is also valid.

We extend this theory to obtain slightly different results which are in better agreement with experiment. The exact expression for χ_{yy} according to Fedders and Martin is

$$\chi_{yy} = \frac{2\mu_B^2}{(2\pi)^3}\int d^3k\,\frac{\partial}{\partial E}\,(\tanh\tfrac{1}{2}\beta E), \tag{5}$$

where μ_B is the Bohr magneton,

$$E^2 = \epsilon^2 + g^2\,,$$

and (6)

$$\epsilon = v(k - k_c),$$

$$\beta = 1/k_BT.$$

The quantity g is the gap function, v is the Fermi velocity, k_c the radius of electron (hole) Fermi sphere, k the magnitude of the wave vector, and k_B the Boltzmann constant. The corresponding expression for the component χ_{zz} derived by Fedders and Martin is

$$\chi_{zz} = \frac{2\mu_B^2}{(2\pi)^3}\left[\int d^3k\left(\frac{g^2}{E^3}\tanh\tfrac{1}{2}\beta E - \frac{g^2}{E^2}\frac{\partial}{\partial E}\right.\right.$$
$$\left.\left.\times(\tanh\tfrac{1}{2}\beta E)\right) + \int d^3k\,\frac{\partial}{\partial E}\,(\tanh\tfrac{1}{2}\beta E)\right]. \tag{7}$$

By differentiating the gap equation, Eq. (7) can be reduced to the form

$$\chi_{zz} = \left(1 + \frac{g}{\beta}\frac{d\beta}{dg}\right)\chi_{yy}\,. \tag{8}$$

In the high-temperature regime below T_N, the second term is negligible and

$$\chi_{yy} \approx \chi_{zz} \approx \chi_{xx} \approx \chi_0[1 + \tfrac{1}{3}\pi^2(k_BT/vk_c)^2]\,, \tag{9}$$

correct to order $(g/k_BT)^2$. The quantity χ_0 is the Pauli magnetic susceptibility given by

$$\chi_0 = [2\mu_B^2/(2\pi)^3]\,8\pi k_c^2/v\,. \tag{10}$$

One should note that the magnetic susceptibility at T_N is larger than χ_0, i.e., $\chi(T_N) > \chi_0$. To the same order, Fedders and Martin predict only a

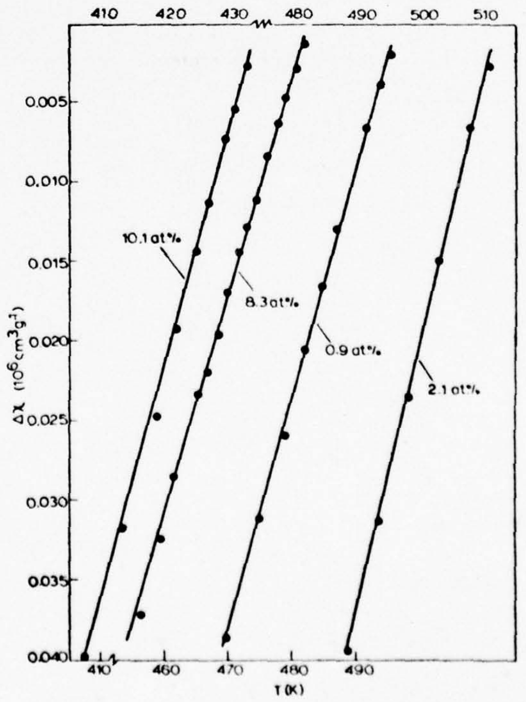


FIG. 4. Δχ as a function of T for chromium-ruthenium alloys containing 0.9-, 2.1-, and 10.1-at.% ruthenium.

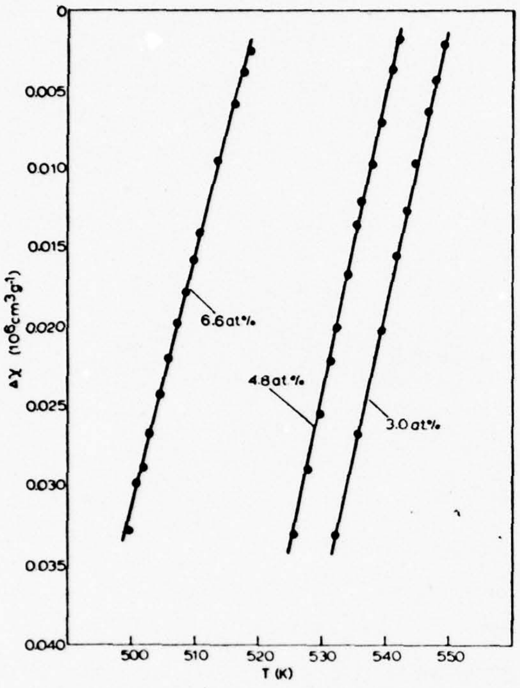


FIG. 5. Δχ as a function of T for chromium-ruthenium alloys containing 3.0-, 4.8-, and 6.6-at.% ruthenium.

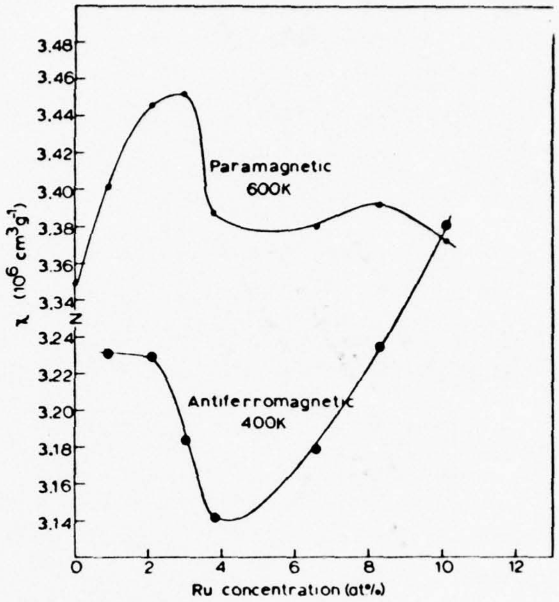


FIG. 6. χ of chromium-ruthenium alloys as a function of ruthenium concentration at 400 and 600 K.

constant term. The second term which is ($\sim k_B T/d$ - band width)^2 represents a correction of only about 1.0%. Nevertheless, this term is vital to a proper interpretation of the experimental results.

Equation (9) implies that the quantity $\Delta\chi = \chi(T_N) - \chi$ (where χ is the magnetic susceptibility below T_N), representing the decrease in χ below T_N, should be proportional to T^2. Since g is only about 0.02 eV even at absolute zero, this conclusion should hold down to about room temperatures. Figure 3 shows $\Delta\chi$ as a function of T^2. It can be seen that these plots are approximately straight lines except for small curvatures below about 350 K. Figures 4 and 5 show $\Delta\chi$ as a function of T just below T_N. These plots indicate that about 20 K below T_N, $\Delta\chi$ is proportional to T, as would be expected from a Taylor expansion near T_N using the above extension of the Fedder-Martin theory. Thus, it appears that this theory accounts reasonably well for the observed temperature dependence of χ of chromium-ruthenium alloys below T_N.

In general, the total value of χ at some particular temperature above T_N of chromium-ruthenium alloys should be made up of the diamagnetic contribution of the closed shells constituting the core of each atom, the diamagnetism due to the conduction electrons in s and d bands, the Van Vleck susceptibility due to the orbital motion of the d electrons, and the Pauli paramagnetic susceptibility. The last contribution is related to the density of states at the Fermi energy. Figure 5 shows the total χ of chromium-ruthenium alloys in the paramagnetic region at 600 K as a function of the ruthenium concentration. Whether the features of this curve are related to the density of states values is difficult to say because of the other magnetic contributions mentioned above. It should be mentioned that various oscillations in the χ-vs-concentration curve have been seen in the chromium-vanadium system,[13] and have been, at least partially, related to the electronic structure of the system. Figure 6 also

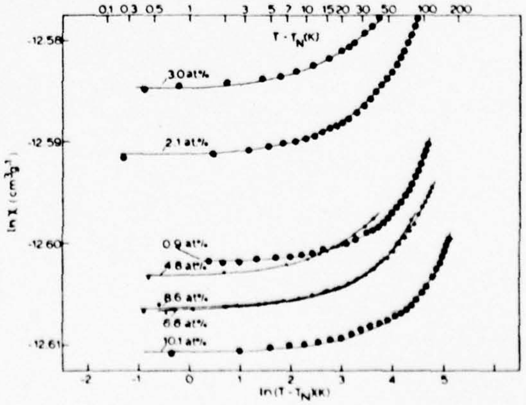


FIG. 7. lnχ as a function of $\ln(T - T_N)$ for chromium-ruthenium alloys above T_N.

presents χ of chromium-ruthenium alloys in the antiferromagnetic state at 400 K. The behavior of this curve is completely different from that in the paramagnetic case. The reasons for the observed minimum at about 5-at.% ruthenium are not understood at this time.

In principle, it would be interesting to determine the critical exponents, characterizing the antiferromagnetic-paramagnetic transitions of the chromium-ruthenium system. Unfortunately, this requires very accurate determination of T_N. Our χ studies indicate that this is difficult to do for the chromium-ruthenium alloys. It is well known that the paramagnetic susceptibility of ferromagnets above the ferromagnetic Curie temperature T_C can be represented by a power law of $T - T_C$. For example, iron obeys such a law[14] with the exponent close to $-\frac{4}{3}$. Phenomenologically, the paramagnetic behavior of χ of the chromium-ruthenium alloys can be analyzed in this fashion. Figure 7 shows $\ln\chi$ vs $\ln(T - T_N)$ for the chromium-ruthenium alloys above T_N. The values of T_N used in this plot are those given in Table I. From Fig. 7 it can be seen that for temperatures between about 0.3 and 5 K, above T_N, χ for all alloys is proportional to $(T - T_N)^\gamma$, where $\gamma \approx 0.7 \pm 0.2$.

ACKNOWLEDGMENT

The authors are grateful to the Office of Naval Research for their financial support under Grant No. N0014-70-A-0311-0001.

---

[1] S. Arajs, T. F. DeYoung, and E. E. Anderson, J. Appl. Phys. 41, 1426 (1970).

[2] T. F. DeYoung, S. Arajs, and E. E. Anderson, J. Less-Common Metals 32, 165 (1973).

[3] S. Arajs and G. R. Dunmyre, J. Appl. Phys. 37, 1017 (1966).

[4] J. G. Booth, Phys. Status Solidi 7, *K*157 (1964).

[5] D. Bender and J. Müller, Phys. Kondens. Mater. 10, 342 (1970).

[6] S. Arajs, E. E. Anderson, J. R. Kelly, and K. V. Rao, AIP Conf. Proc. (to be published).

[7] L. Hedman, H. U. Åström, K. V. Rao, and S. Arajs, Int. J. Magn. (to be published).

[8] W. C. Koehler, R. M. Moon, A. L. Trego, and A. R. Mackintosh, Phys. Rev. 151, 405 (1966).

[9] M. Zuckermann, Phys. Lett. A 31, 362 (1970).

[10] P. A. Fedders and P. C. Martin, Phys. Rev. 143, 245 (1966).

[11] K. Maki and M. Sakurai, Prog. Theor. Phys. 47, 1110 (1972).

[12] M. Crisan, Phys. Rev. 9, 4838 (1974).

[13] B. G. Childs, W. E. Gardner, and J. Penfold, Philos. Mag. 5, 1267 (1960).

[14] S. Arajs and R. V. Colvin, J. Appl. Phys. 35, 2424 (1964).

16

MAGNETIC SUSCEPTIBILITY OF Ni-Aℓ ALLOYS AT HIGH TEMPERATURES

Sigurds Arajs and J.R. Kelly
Department of Physics
Clarkson College of Technology
Potsdam, New York 13676

ABSTRACT of this analysis is that there are localized mome

[illegible]

Reprinted from

AIP Conference Proceedings
No. 29

Magnetism and Magnetic Materials—1975

(21st Annual Conference–Philadelphia)

Edited by
J. J. Becker, G. H. Lander, J. J. Rhyne

American Institute of Physics

MAGNETIC SUSCEPTIBILITY OF Ni-Aℓ ALLOYS AT HIGH TEMPERATURES

Sigurds Arajs and J.R. Kelly
Department of Physics
Clarkson College of Technology
Potsdam, New York 13676

ABSTRACT

The mass magnetic susceptibility (χ) has been determined as a function of temperature (T) of binary Ni-Aℓ alloys, containing 2.1, 4.2, 6.5, 8.7, 11.5 and 16.2 at. % Aℓ, between their ferromagnetic Curie temperatures (T_C) and 1500 K. The χ data satisfy the modified Curie-Weiss law, $\chi = C/(T-\theta)+\chi_0$, where C,$\theta$, and χ_0 are constants, between T' and 1500 K. The temperature T' is some minimum temperature which decreases with increasing Aℓ content. The above constants give additional support to the recent interpretation of paramagnetism by Beck and Flynn, postulating the existence of localized magnetic moments up to 1500 K.

INTRODUCTION

At the present time there are no satisfactory theories for the paramagnetic state of ferromagnetic materials involving the transition elements. Neither Fe or Ni or Co satisfy the Curie-Weiss law,

$$\chi = C/(T-\theta) \ , \qquad (1)$$

or the modified Curie-Weiss law,

$$\chi = C/(T-\theta) + \chi_0, \qquad (2)$$

where χ is the magnetic susceptibility, T the absolute temperature, and C,θ, and χ_0 are constants over the whole paramagnetic solid state region. Recently Beck and Flynn[1] have suggested that the paramagnetic behavior of Ni above the ferromagnetic Curie temperature (T_C) is strongly influenced by the short-range magnetic order effects which can exist up to at least 1000K.[2] Furthermore, they have found that χ data of Ni[3] can be fitted very satisfactorily to Eq. 2 between 1000 and 1500 K. From the value of C and the assumption that the g-factor is equal to 2, they conclude that the magnetic moment on Ni atoms is about 0.7 μ_B which they compared with the ferromagnetic moment of 0.6 μ_B. The major implication of this analysis is that there are localized moments on Ni atoms in the paramagnetic state at elevated temperatures. The purpose of the present investigations is to present new high temperature χ measurements on Ni-Aℓ alloys and to analyze them from the viewpoint mentioned above.

EXPERIMENTAL CONSIDERATIONS

The Ni-Aℓ alloys used in this study were prepared by levitation melting using Johnson and Matthey Ni and Aluminum Corporation of America Aℓ. The metallurgical procedures used for making these alloys are very similar to those described elsewhere.[4] The χ data were measured by means of the apparatus, based on the Faraday method, similar to that used before.[3]

RESULTS AND DISCUSSION

The behavior of $1/\chi$ of Ni and Ni-Aℓ alloys, containing 2.1, 4.2, 6.5, 8.7, 11.5, and 16.2 at. % Aℓ, as a function of T up to 1500 K is shown in Fig. 1. All curves exhibit a downward curvature with respect to the T axis characteristic to Ni alloys. We have found that it is impossible to fit the χ data to Eq. 2 above T_C (neglecting the magnetic effects just above T_C associated with the critical aspects of the transition) and 1500 K with χ_0 as a constant. However, if we assume that magnetic short-range effects extend to high temperatures to some limiting temperature T', then above T' the experimental χ data for all Ni-Aℓ alloys satisfy Eq. 2. Because T_C decreases with increasing Aℓ concentration, T' also decreasing in a similar fashion. We have found from our computer analysis on pure Ni that when T' = 1000 K, C = 3.98 $10^{-3} cm^3 Kg^{-1}$. This value of C implies that the effective paramagnetic moment $\mu_{eff}^{Ni} = g[S(S+1)]^{1/2} = 1.36\ \mu_B$, where μ_B is the Bohr magneton and S the spin quantum number. If g = 2 (as was assumed by Beck and Flynn[1]), then $\mu^{Ni} = gS = 0.698\ \mu_B$. This value is in good agreement with that

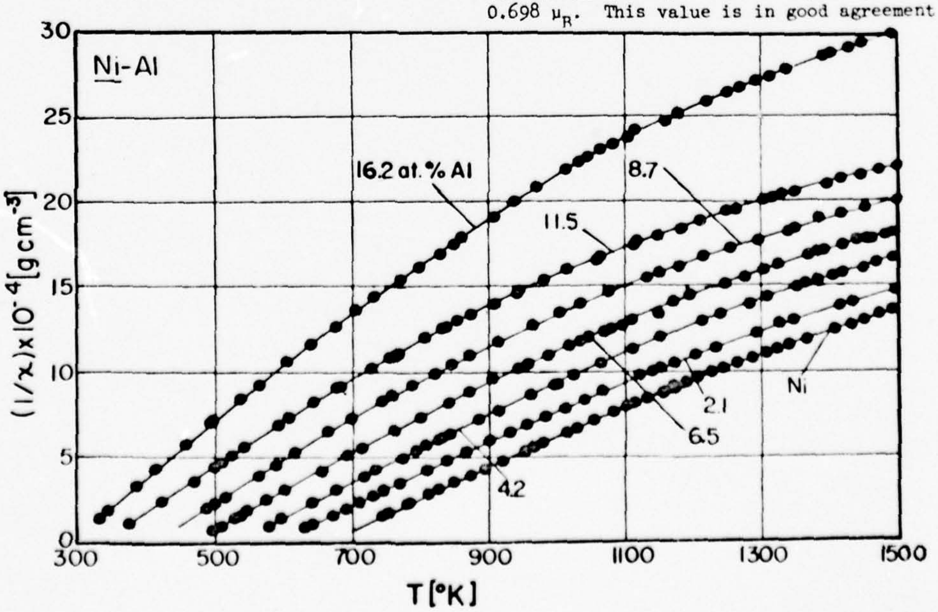


Fig. 1. Inverse Magnetic Susceptibility of Ni-Aℓ Alloys

calculated by Beck and Flynn.[1] A similar computer analysis has been carried out on all our Ni-Aℓ alloys, with T' gradually decreasing to almost 800 K for the 16.2 at. % Aℓ sample. Figure 2 shows the computer plots of $1/(\chi-\chi_0)$ as a function of T which clearly illustrate the linearity at elevated temperatures. If the quantities C, determined from the linear portions of Fig. 2, are analyzed in a manner similar to the Ni case, we find that the paramagnetic moments per Ni atom μ_{eff}^{Ni}, and hence (assuming $g = 2$) also the paramagnetic μ^{Ni} gradually decrease with increasing Aℓ content. For pure Ni the quantity μ^{Ni}, obtained from the paramagnetic high T data, is about 0.1 μ_B larger than the corresponding ferromagnetic moment. The reasons for this discrepancy are not clear at the present time. It is interesting to note that our values of μ^{Ni} (which for space purposes are not presented in detail here), calculated from the χ data at high T, form a straight line with respect to the Aℓ concentration, which is approximately parallel to the μ^{Ni} line obtained from the ferromagnetic data[5-8]. The difference of about 0.1 μ_B, observed for pure Ni, appears to remain the same also for the Ni-Aℓ alloys.

In summary, our χ results on Ni-Aℓ alloys can be fitted to Eq. 2 at elevated temperatures. The values of the constants support the ideas of Beck and Flynn[1] that localized magnetic moments exist in Ni-Aℓ alloys up to 1500 K.

ACKNOWLEDGMENTS

This work has been supported by the Office of Naval Research under Grant Number N0014-70-A-0311-001. The authors are grateful to Professor P.A. Beck for his preprint of Reference 1 and for reopening our interest in the high temperature behavior of ferromagnetic transition metals.

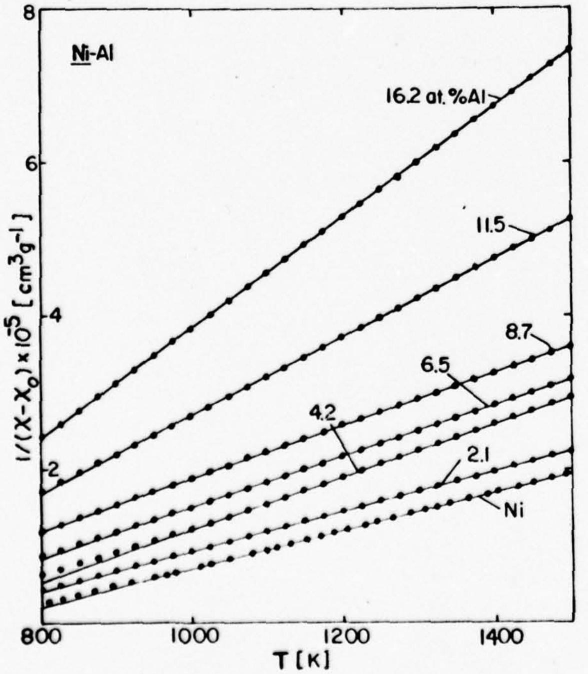


Fig. 2. $1/(\chi-\chi_o)$ as a function of temperature for Ni-Aℓ alloys

REFERENCES

1. P.A. Beck and C.P. Flynn (to be published in Sol. State Commun).
2. M. Braun and R. Kohlhaas, phys. stat. sol. 12, 429 (1965).
3. S. Arajs and R.V. Colvin, J. Phys. Chem. Solids 24, 1233 (1963).
4. H. Chessin, S. Arajs, and R.V. Colvin, J. Appl. Phys. 35, 2419 (1964).
5. C. Sadron, Ann. phys. 17, 371 (1932).
6. V. Marian, Ann. phys. 7, 459 (1937).
7. W. Sucksmith, Proc. Roy. Soc. (London) A171, 525 (1939).
8. J. Crangle and M.J.C. Martin, Phil. Mag. 4, 1006 (1959).

17

short note

reprinted from

physica
status
solidi (b)

phys. stat. sol. (b) 74, K23 (1976)

Subject classification: 18.4; 21.1

Department of Physics, Clarkson College of Technology, Potsdam, New York

Antiferromagnetic Susceptibility of Cr-Re Alloys

By

A. ARAJS, G. KOTE, C.A MOYER, J.R. KELLY, K.V. RAO,
and E.E. ANDERSON

Introduction The temperature dependence of χ of binary Cr alloys is a relatively unexplored subject from both experimental and theoretical viewpoints. According to the two-band model of Fedders and Martin (1), the quantity χ (to the first order of their calculation) of Cr above T_N should be constant. Below T_N, χ is depressed because of the energy gap which keeps the spins in an antiferromagnetically ordered spin density wave. The theory of Fedders and Martin predicts that just below T_N, the quantity $\Delta\chi = \chi(T_N) - \chi(T)$ should be proportional to T. Recently we have extended the above theory by evaluating essentially exactly the integrals describing the temperature dependence of the perpendicular and parallel components of χ in the antiferromagnetic region (2), (3). To lowest order in the gap energy these new calculations predict that $\Delta\chi$ for an itinerant electron antiferromagnet without localized magnetic moments should decrease as T^2. The purpose of this paper is to test this prediction on the Cr-Re system whose magnetic structures (4), electrical resistivity (5), (6) and the behavior of T_N (7) have been explored before.

Experimental considerations The Cr-Re samples used for the χ studies were cut from arc melted ingots (about 8.0x0.7x0.6 cm^3). These melts were made using Cr from Chromalloy Corporation and Re from Engelhard Industries, Inc. according to our standard procedures described elsewhere (8). The χ data were obtained using the apparatus (2) based on the Faraday method.

Results and discussion The behavior of χ of Cr and Cr alloys containing 0.56, 2.45, 5.05, 6.52, 10.7, and 13.1 at% Re as a function of T is shown in Fig. 1. The arrows in this figure indicate that the antiferromagnetic transition temperature increases rapidly with increasing Re concentration, reaching a maximum of about 575 K at 7 at% Re and then decreases with further additions of Re. The values of T_N, determined from enlarged χ versus T plots, are summarized

Table 1

T_N of Cr-Re alloys

Re concentration (at%)	T_N(K)
0	
0.56	416±4
2.45	562±3
5.05	573±3
6.52	575±3
10.7	572±4
13.1	492±4

in Table 1. These values are in good agreement with those determined from the *electrical resistivity* (*ϱ*) *curves by locating* temperatures at which dϱ/dT is minimum.

It is obvious from Fig. 1 that the onset of antiferromagnetism decreases χ in all the samples used in this investigation except the Cr-Re specimen containing 13.1 at% Re. The decrease $\Delta\chi$ below T_N is presented in Fig. 2 as a function of T^2, including an insert where $\Delta\chi$ is shown near T_N as a function of T. Experimental results clearly indicate that just below T_N $\Delta\chi$ is proportional to T. At lower temperatures $\Delta\chi$ varies as T^2. This behavior is predicted from the extension of the Fedders and Martin theory mentioned above. Specifically, we find that below T_N to zeroth order in the spin density wave gap,

$$\chi(T) = \chi_o \left[1 + \frac{1}{3x_N^2} \left(\frac{T}{T_N} \right)^2 \right],$$

where $x_N = (1/\pi)\beta_N vK_c$ and χ_o is the

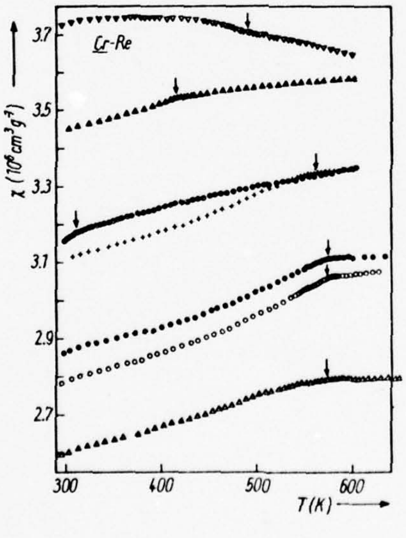
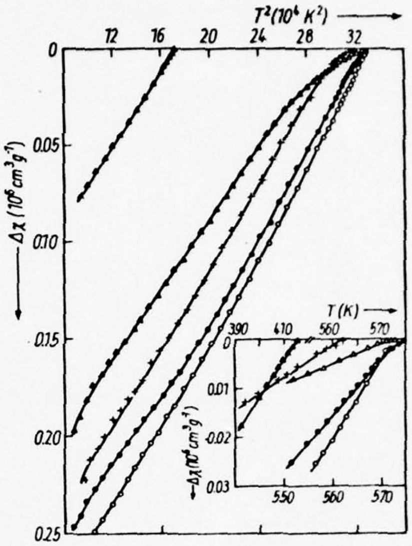


Fig. 1. χ as a function of T. ▿ 13.1 at% Re, ▲ 0.56 at% Re, ⊖ Cr, + 2.45 at% Re, ● 6.52 at% Re, ○ 5.05 at% Re, △ 10.7 at% Re

Fig. 2. $\Delta\chi$ as a function of T^2 and T. ▲ 0.56 at% Re, △ 10.7 at% Re, + 2.45 at% Re, ● 6.52 at% Re, ○ 5.05 at% Re



Pauli magnetic susceptibility. The quantity $\beta_N = (k_B T_N)^{-1}$, where k_B is the Boltzmann constant, v is the Fermi velocity, and K_c the radius of the electron (hole) Fermi surface. Although the experimental values of $\Delta\chi$ versus T^2 do not form perfect straight lines, it definitely appears that $\Delta\chi$, at least approximately, follows the T^2 prediction down to 300 K. The T dependence just below T_N shown in the insert of Fig. 2, is simply a result expected from the Taylor expansion of $\chi(T)$ about T_N. Also, it should be noted that the predicted $\chi(T_N)$ exceeds χ_o, in contrast to the Fedders-Martin result. Actually, the larger value should have been anticipated, since the existence of a spin density wave below T_N presupposes electron correlations which are neglected in the calculation of the Pauli term. Inclusion of these correlations would enhance the spin susceptibility over the non-interacting value by a factor specified by some average effective exchange coupling between electrons. Thus, it appears that the modified theory accounts reasonably well for the observed temperature dependence of χ of Cr-Re alloys between 300 K and T_N.

The behavior of χ of the alloy containing 13.1 at% Re is completely different from the other samples (Fig. 1). In this case χ increases with T below T_N reaching a flat maximum at about 375 K. The present theory is unable to account for this behavior. Furthermore, it should be noted that χ is not constant above T_N as expected from the Fedders and Martin theory. In fact, χ in general increases (except for the 13.1 at% Re sample) quite strongly with T. These observations above T_N and the χ behavior at low temperatures are being studied further theoretically and experimentally at the present time.

Acknowledgements

This work has been supported by the Office of Naval Research under Grant Number ND014-70-A-0311-0001. Helpful discussions with Prof. H.U. Åström from the Royal Institute of Technology, Sweden are greatly appreciated. We also would like to acknowledge interesting correspondence with Dr. M. Crisan from Cluj University, Romania.

References

(1) P.A. FEDDERS and P.C. MARTIN, Phys. Rev. 143, 245 (1966).
(2) S. ARAJS, C.A MOYER, J.R. KELLY, and K.V. RAO, Phys. Rev., October issue 1975.
(3) C.A. MOYER, S. ARAJS, L. HEDMAN, H.U. ÅSTRÖM, and K.V. RAO, unpublished investigations.
(4) W.C. KOEHLER, R.M. MOON, A.L. TREGO, and A.R MACKINTOSH, Phys. Rev. 151, 405 (1966).
(5) A.L. TREGO and A.R. MACKINTOSH, Phys. Rev. 166, 495 (1968).
(6) D. ABUKAY, K.V. RAO, and S. ARAJS, unpublished investigations.
(7) J.G. BOOTH, phys. stat. sol. 7, K157 (1964).
(8) S. ARJAS, Canad. J. Phys. 47, 1005 (1969).

(Received December 10, 1975)

18

Accepted for publication by J. Magn. Magn. Material. Will be published in 1976.

ELECTRICAL RESISTIVITY OF IRON-VANADIUM ALLOYS BETWEEN 78 AND 1200 K

by

W. Teoh, Sigurds Arajs, D. Abukay, and E.E. Anderson
Department of Physics
Clarkson College of Technology
Potsdam, New York 13676

ABSTRACT

Electrical resistivity (ρ) of Fe-V alloys containing 0.5, 0.9, 2.7, and 6.1 at.% V has been measured as a function of temperature (T) between 78 and 1200 K. The ρ vs. T curves exhibit a change in the slope at the ferromagnetic Curie temperature (T_c). The $d\rho/dT$ vs. T curves in the neighborhood of T_c are similar to the corresponding plot for pure Fe. Our studies confirm the previously observed anomalous effect of V on T_c of Fe, i.e., that T_c increases with small additions of V to Fe. The critical index λ^+ associated with the power law of $d\rho/dT$ just above T_c has been determined as a function of V concentration.

INTRODUCTION

Alloying Fe with V gives rise to unusual magnetic properties. First, the ferromagnetic Curie temperature (T_c) increases with increasing V content reaching a maximum value at about 10 at.% V according to the most recent work[1]. Second, the addition of V to the bcc Fe lattice increases its paramagnetic susceptibility (χ).[2] The maximum in the χ vs. at.% V curve decreases with increasing temperature (T). At 1160 K this maximum also occurs at about 10 at.% V. These unique results, which appear to be independent of heat treatments and the mode of temperature changes have stimulated us to explore other physical properties of the Fe-V system, especially in the neighborhood of T_c, in order to see whether they also behave anomalously in comparison with those of other binary iron alloys. In this paper we describe detailed investigations of the electrical resistivity (ρ) of low concentration Fe-V alloys as a function temperature and discuss the significance of the results.

EXPERIMENTAL PROCEDURES

The Fe-V alloys containing 0.5, 0.9, 2.7, and 6.1 at.% V, were prepared by a levitation melting technique using Fe obtained from Johnson-Matthey and Company (Cat. No. 849) and V from Electrometallurgical Company. The alloys, produced in the form of rods of diameter 0.5 cm and length 7 cm were homogenized in silicon tubes at about 1400 K for 12 hours. The homogeneity was confirmed by metallographic examinations. The electrical resistivity samples (approximate dimensions: length 3.0 cm, diameter 0.3 cm) were modelled from the above ingots. Before the electrical transport property studies these samples were vacuum-annealed at 900 K for 4 hours and then cooled to room temperatures in about 10 minutes.

The electrical resistivity between 78 and 330 K was determined using the facilities described elsewhere.[3] The measurements from room temperature to 1200 K were made in a Pt vacuum furnace using the four-probe method. Spotwelded Mo wires (diameter 0.038 cm) served as potential and current leads. The temperatures were measured by a Pt and Pt-10 % Rh thermocouple.

RESULTS AND DISCUSSION

It is well-known that measurements of the residual electrical resistivity as a function of solute concentration provide a useful check on the quality of a particular binary system of solid solutions. Figure 1 shows the values of ρ at 4.2 K of the Fe-V alloys used in this study. The initial increase in the electrical resistivity is about 1.2 $\mu\Omega$ cm per 1 at.% V, in good agreement with the value determined in another investigation.[4] However, it should be remarked that our values at 4.2 K appear to be slightly higher than those determined by Sueda et al.[1] They also observed an inflection point in the ρ vs. at% V curve at about 10 at.% V.

Figure 2 shows the electrical resistivity of Fe and our Fe-V alloys containing 0.5, 0.9, 2.7, and 6.1 at.% V between 78 and 1200 K. The curve for pure Fe was not determined in this study. The portion of the ρ vs. T curve above 300 K has been plotted using data reported elsewhere.[5] The data below 300 K are due to McElroy from Oak Ridge National Laboratory.[6]

At elevated temperatures each of the ρ vs. T curves undergo an abrupt slope change which results from a ferromagnetic-paramagnetic transition. Details of this behavior are shown in Figure 3. In general, this behavior is typical for binary Fe alloys except for an anomalous effect of V on T_c of Fe. Figure 4 presents $d\rho/dT$ vs. T of Fe-V alloys in the neighborhood of the Curie temperature

T_c, which can be determined from such plots as the temperature at which $d\rho/dT$ diverges. The $d\rho/dt$ vs. T plots for the above alloys are very similar to the corresponding curve for pure Fe.[7] The values of T_c, determined from such plots, are shown in Figure 5 in comparison with some previous measurements of T_c on Fe-V alloys.[1,8] Our results confirm the increase in T_c of Fe with V concentration. All the known results on the Fe-V system prior to 1934 have been carefully reviewed by Edlund.[8] The earlier determinations[9-13] of T_c, which contain many inconsistencies, have been interpreted by Edlund as resulting primarily from improper alloy preparations and impure samples. The principal results of Edlund's work is the unusual effect of V on T_c of Fe. The T_c of Fe-V alloys increases with V concentrations, reaching a maximum at about 12 at.% V, and then falls off with further additions of V. According to Edlund, the initial increase in T_c is 0.13 K per 0.01 at.% V up to 1.2 at.% V, while we obtain a value of about 1.0 K per 0.01 at.%V. After Edlund's studies, Fallot[14] published his work on the saturation magnetization at room temperatures and T_c of Fe-V alloys. According to Fallot, V also initially increases T_c with increasing V content, the maximum occurring at about 8 at.% V. Quantitatively, Fallot's results for T_c are not in good agreement with those of Edlund, especially at higher V concentrations. A more recent study of dilute Fe-V alloys is due to Arott,[15] who finds that small amounts of V increase T_c of Fe and that the magnetic moment per Fe atom remains essentially constant. The most recent contribution on the behavior of T_c of Fe-V alloys is by Sueda et al.[1] These investigators determined the values of T_c from the electrical resistivity curves using the method of $d\rho/dT$ maximum. At low composition, their values appear to be slightly higher than those of Edlund and the present study. This discrepancy, however, disappears at 10 at.% V level.

At the present time there is no satisfactory theory for the unusual effect of V on T_c of Fe. It should be noted from Figure 5 that there is also a maximum in the T_p vs. V concentration curve,[2] where T_p is paramagnetic Curie temperature. Recently Huffman[16] has calculated the variation of T_c with composition for binary alloys containing Al, Si, Ge, Zn, and Sn. By using a molecular field theory including the concentration effects of the indirect (RKKY) exchange interaction, he has been able to obtain a good agreement between his theory and experimental results including even the Fe-Ge system. According to Arajs,[17] the curve of T_c vs. Ge concentration shows a small maximum at about 1.5 at.% Ge, which is an unusual effect. It would be of interest to apply Huffman's theory also to the Fe-V system in order to see whether the maximum in the T_c curve can also be explained by means of this model.

According to Shacklette[17] pure Fe obeys a power law just below and above T_c,

$$\frac{d\rho}{dT} = \frac{A^{\pm}}{\lambda^{\pm}} (\varepsilon^{-\lambda^{\pm}} - 1) + B^{\pm} \text{ and } \varepsilon = |T - T_c|/T_c,$$

where $A^{\pm}$ and $B^{\pm}$ are constants and $\lambda^{\pm}$ are the critical exponents. The plus sign refers to $T>T_c$, the minus sign to $T<T_V$. Shacklette finds that $\lambda^{\pm} = \lambda^{-} = -0.120 \pm 0.01$ and that, furthermore, $d\rho/dT$ scales in the same manner as the magnetic specific heat. The only other determination of $\lambda^{\pm}$ for Fe are due to Kraftmakher and his coworkers[18,19] and Nagy and Pál.[20] According to Kraftmakher $\lambda^{\pm} \approx 0 \pm 0.1$, i.e., the divergence is essentially logarithmic. On the other hand, Nagy and Pál find that $\lambda^{+} = 0.4 \pm 0.1$ for $10^{-3} \lesssim \varepsilon \lesssim 3.3\ 10^{-3}$. In short, the presently available values on $\lambda^{\pm}$ of pure Fe are not consistent with each other.

It is reasonable to assume that $d\rho/dT$ of Fe-V alloys could also be described by the above power law. If this is the correct assumption, than a plot of $\ln(d^2\rho/dT^2)$ vs. $\ln \varepsilon$ should be a straight line whose slope is $-(\lambda^{\pm}+1)$. Our data of ρ vs. T of Fe-V alloys in the neighborhood of T_c are not of sufficiently high quality for obtaining $d^2\rho/dT^2$ values of the accuracy calculated by Shatcklette.[17] However, since there are no previous determinations of $\lambda^{\pm}$ for ferromagnetic alloys, we have made attempts to obtain these exponents from our data. Unfortunately the plots of $\ln d^2\rho/dT^2$ vs. $\ln \varepsilon$ for $T<T_c$ exhibit considerable scatter so that no reliable λ^- can be determined. Above T_c the same type plots form approximately straight lines for $10^{-2} \lesssim \varepsilon \lesssim 3\ 10^{-3}$. A typical plot for the Fe-V alloy containing 2.7 at.% V is shown in Figure 6. The slope of straight line gives $\lambda^+ = 1.0 \pm 0.2$. Figure 7 presents λ^+ as a function V concentration. The solid curve connecting the λ^+ values of Fe-V alloys is based on the assumption that Shacklette's[17] determination of λ^+ for pure Fe is more reliable than the earlier estimates mentioned above. Our results strongly suggest that at least λ^+ is a function of solute concentration. It definitely would be of interest to determine λ^+ and λ^- for other binary Fe alloys using more accurate experimental techniques such as those described in Reference 21. Such studies on high purity Fe and various Fe alloys are in progress.

ACKNOWLEDGMENT

The authors are grateful to the Office of Naval Research for their financial support. Helpful discussions with Professor K.V. Rao and Dr. Y.D. Yao are greatly appreciated.

REFERENCES

1. N. Sueda, Y. Fujiwara, and H. Fujiwara, J. Sci. Hiroshima Univ., Ser. A-II, 33, 267 (1969).
2. S. Arajs, R.V. Colvin, H. Chessin, and J.M. Peck, J. Appl. Phys. 33, 1353 (1962).
3. S. Arajs, Canad. J. Phys. 47, 1005 (1969).
4. S. Arajs, F.C. Schwerer, and R.M. Fisher, phys. stat. sol. 33, 731 (1969).
5. S. Arajs and R.V. Colvin, phys. stat. sol. 6, 797 (1964).
6. D.L. McElroy (private communications).
7. L.W. Shacklette, Phys. Rev. B9, 3789 (1974).
8. D.L. Edlund, "The Magnetic Transformation in Iron-Vanadium Alloys", Ph.D. thesis, Massachusetts Institute of Technology (1934).
9. P. Pütz, Metallurgie 3, 649 (1906).
10. A. Portevin, Rev. Metallurgie 6, 1353 (1909).
11. E. Maurer, Stahl and Eisen 45, 1629 (1925). ←
12. M. Oya, Science Reports Tohoku Imperial University (Series I) 19, 235 (1930).
13. F. Wever and W. Jellinghaus, Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf 12, 317 (1930).
14. M. Fallot, Ann. Phys. 6, 305 (1936).
15. A. Arrott and J.E. Noakes, J. Appl. Phys. 30, 97S (1959).
16. G.P. Huffman, AIP Conf. Proc. 5, 1310 (1972).
17. L.W. Shacklette, Phys. Rev. 9, 3789 (1974).
18. Ya. A. Kraftmakher and T. Yu Romashina, Soviet Phys. Solid State 9, 1459 (1967).
19. Ya. A. Kraftmakher and T. Yu. Pinegina, Soviet. Phys. Solid State 16, 78 (1974).
20. I. Nagy and L. Pál, J. Physique, Cl, Suppl. 2-3, 32, 531 (1971).
21. K.V. Rao, Ö. Rapp, Ch. Johannesson, D.J.W. Geldart, ed. T.G. Richards, J. Phys. C8, 2135 (1975).

CAPTIONS FOR FIGURES

Figure 1 Residual electrical resistivity of Fe-V alloys as a function of V concentration.

Figure 2 Electrical resistivity of Fe-V alloys as a function of temperature between 4.2 and 1200 K.

Figure 3 Electrical resistivity of Fe-V alloys in the neighborhood of the ferromagnetic Curie temperature.

Figure 4 Temperature derivation of the electrical resistivity in the neighborhood of the ferromagnetic Curie temperature.

Figure 5 Ferromagnetic and paramagnetic Curie temperatures of Fe-V alloys as a function of V concentration.

Figure 6 $\ln d^2\rho/dT^2$ vs. $\ln \varepsilon$ of Fe-0.5 at.% V alloy for $T>T_c$.

Figure 7 λ^+ as a function of V concentration.

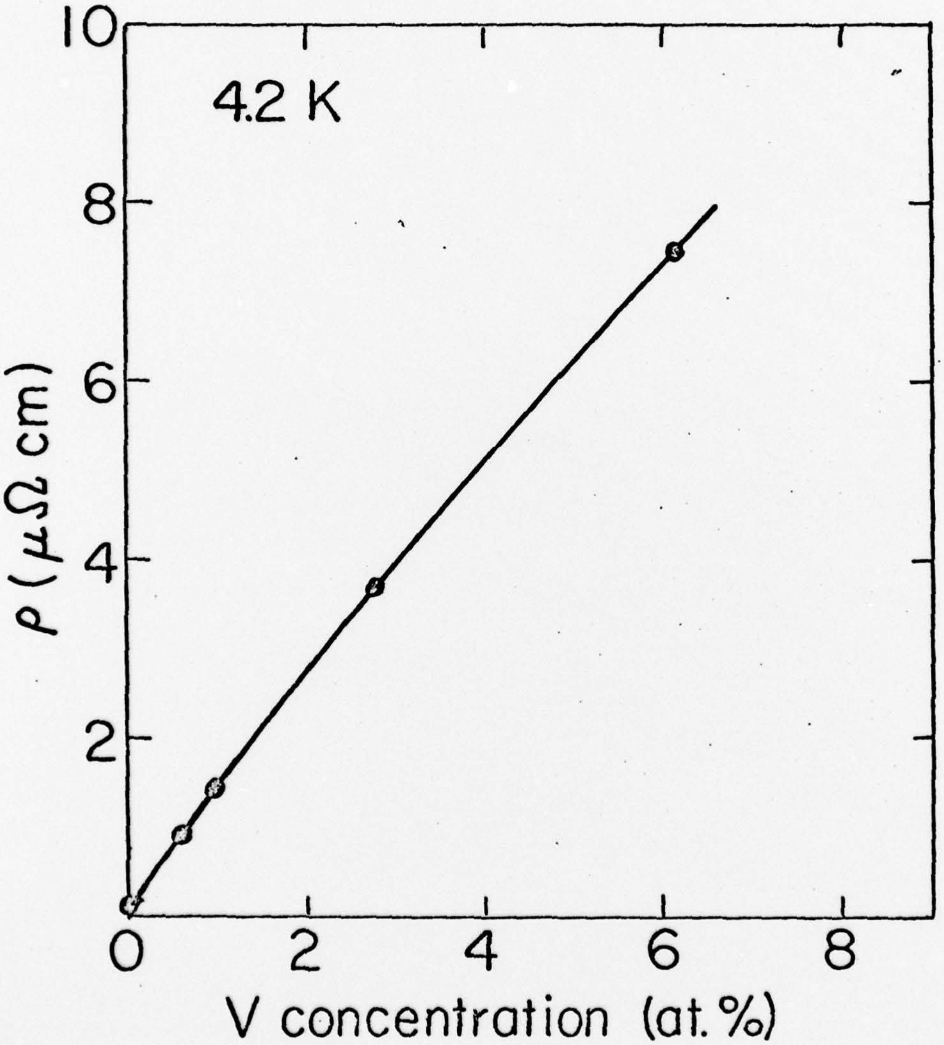
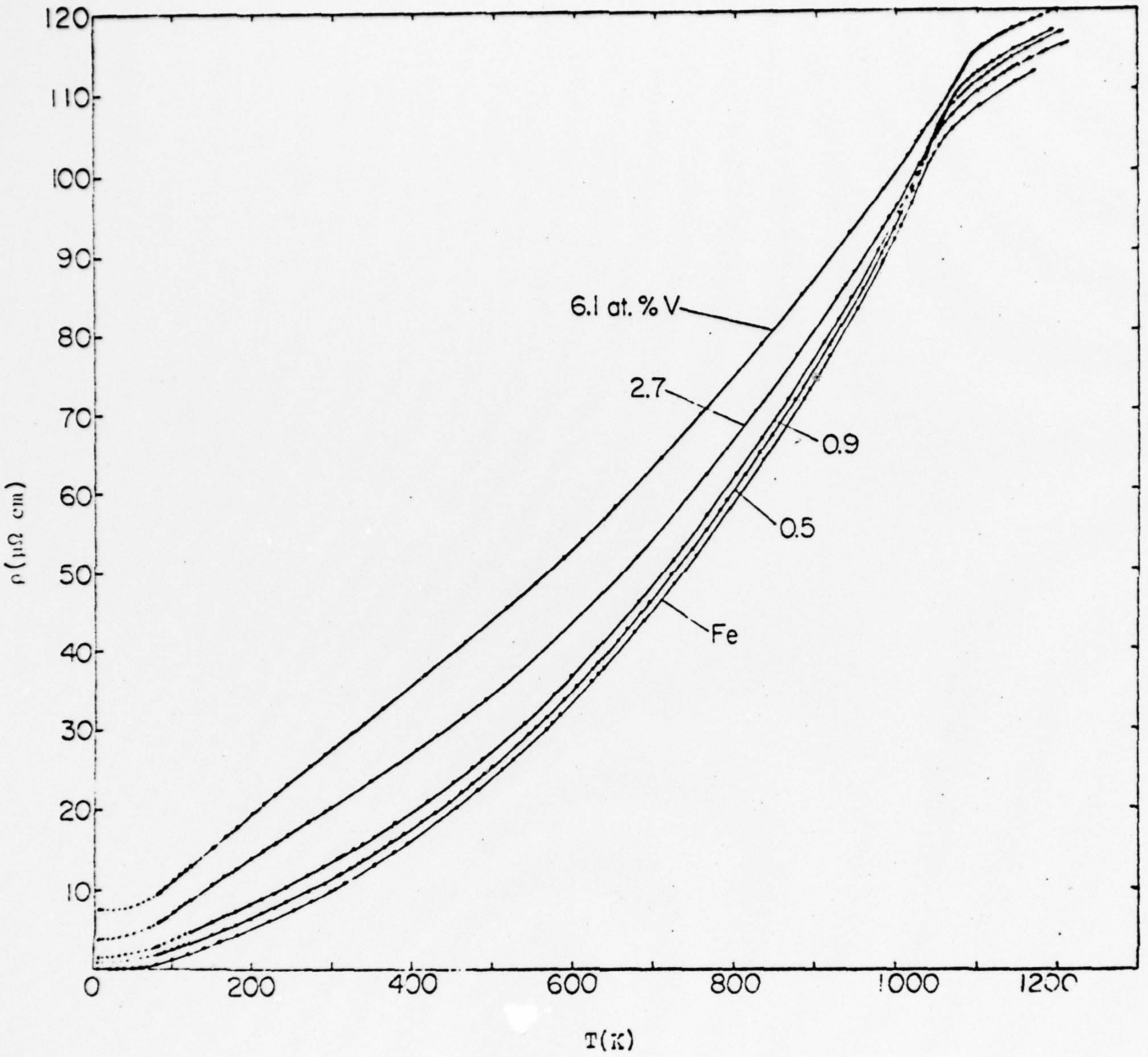


Fig. 1

Teoh et al



120
110
100
90
80
70
60
50
40
30
20
10
ρ(μΩ cm)
0
200
400
600
800
1000
1200
T(K)
6.1 at. % V
2.7
0.9
0.5
Fe

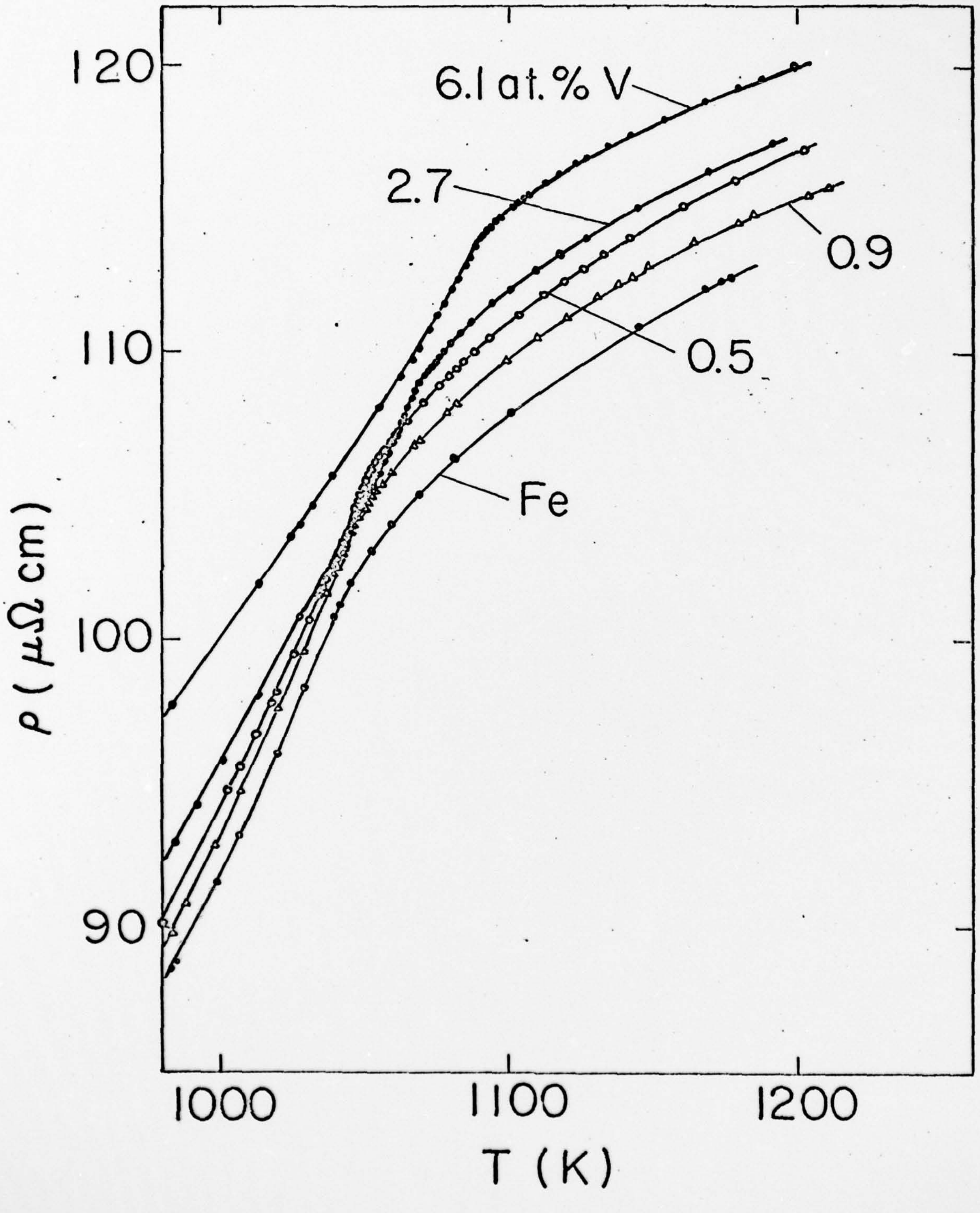
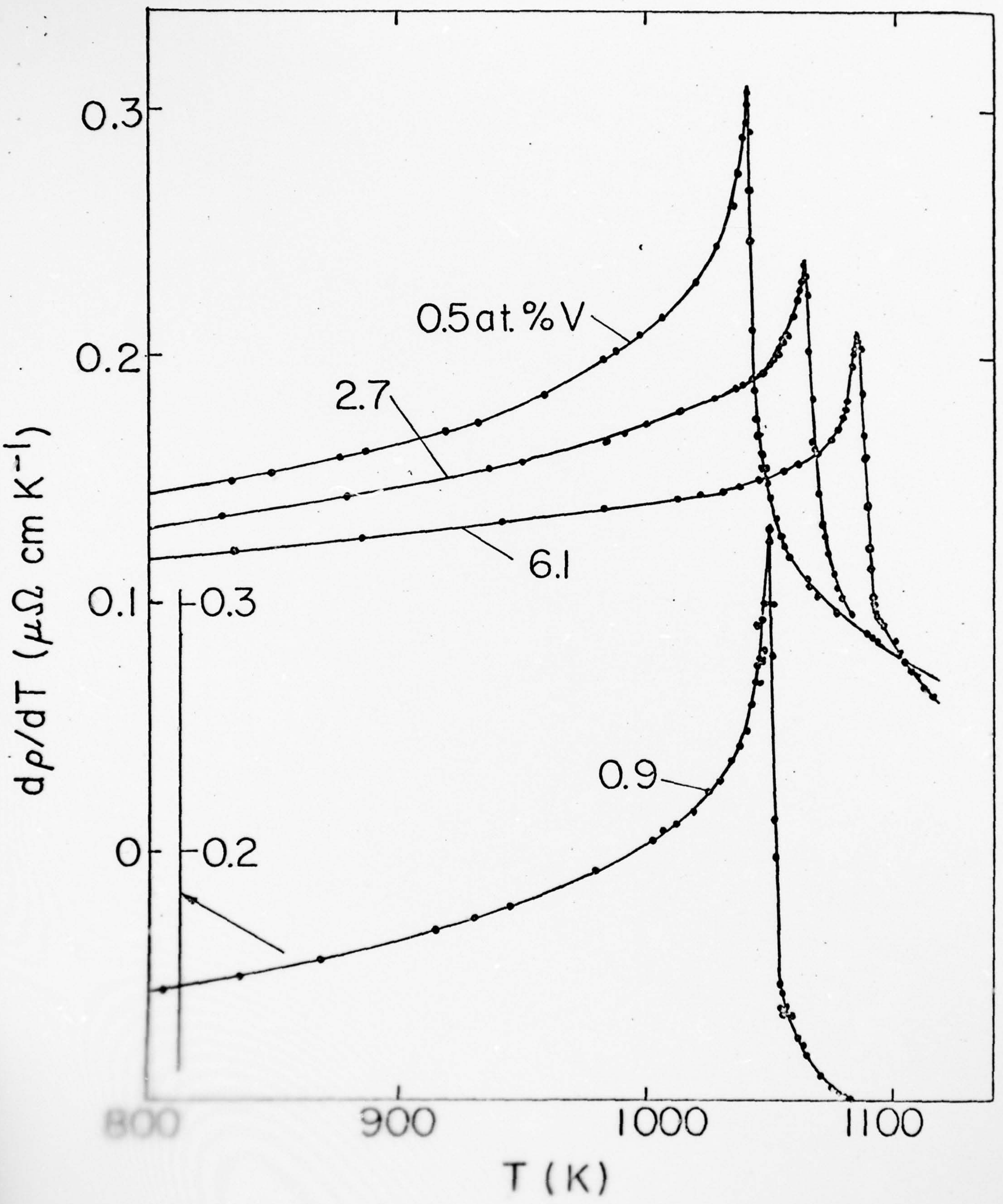
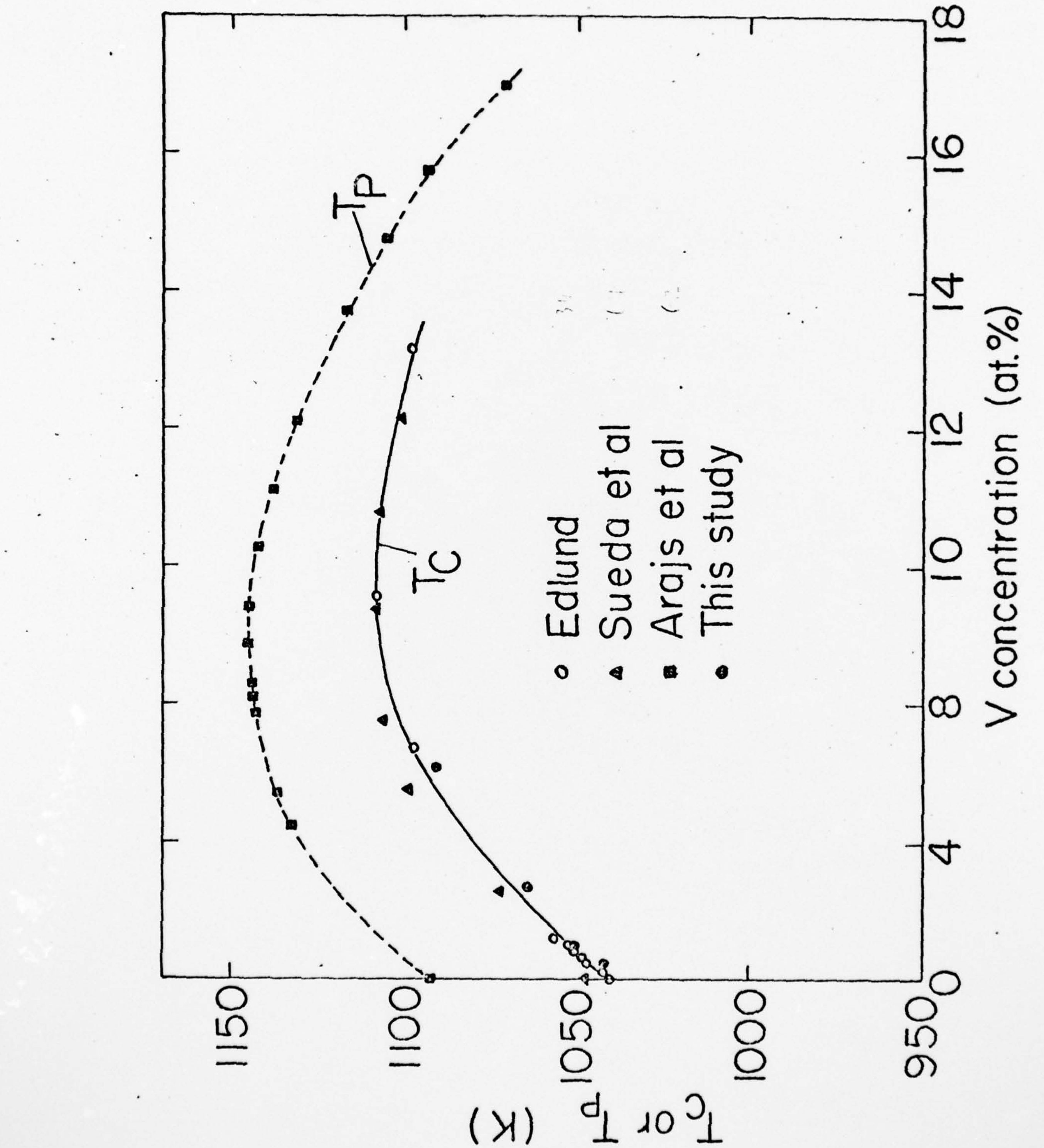


Fig 3

Teoh et al



Tesk et al



T_C or T_P (K)
1150
1100
1050
1000
950
0
4
8
10
12
14
16
18
V concentration (at.%)
T_P
T_C
○ Edlund
▲ Sueda et al
■ Arajs et al
● This study

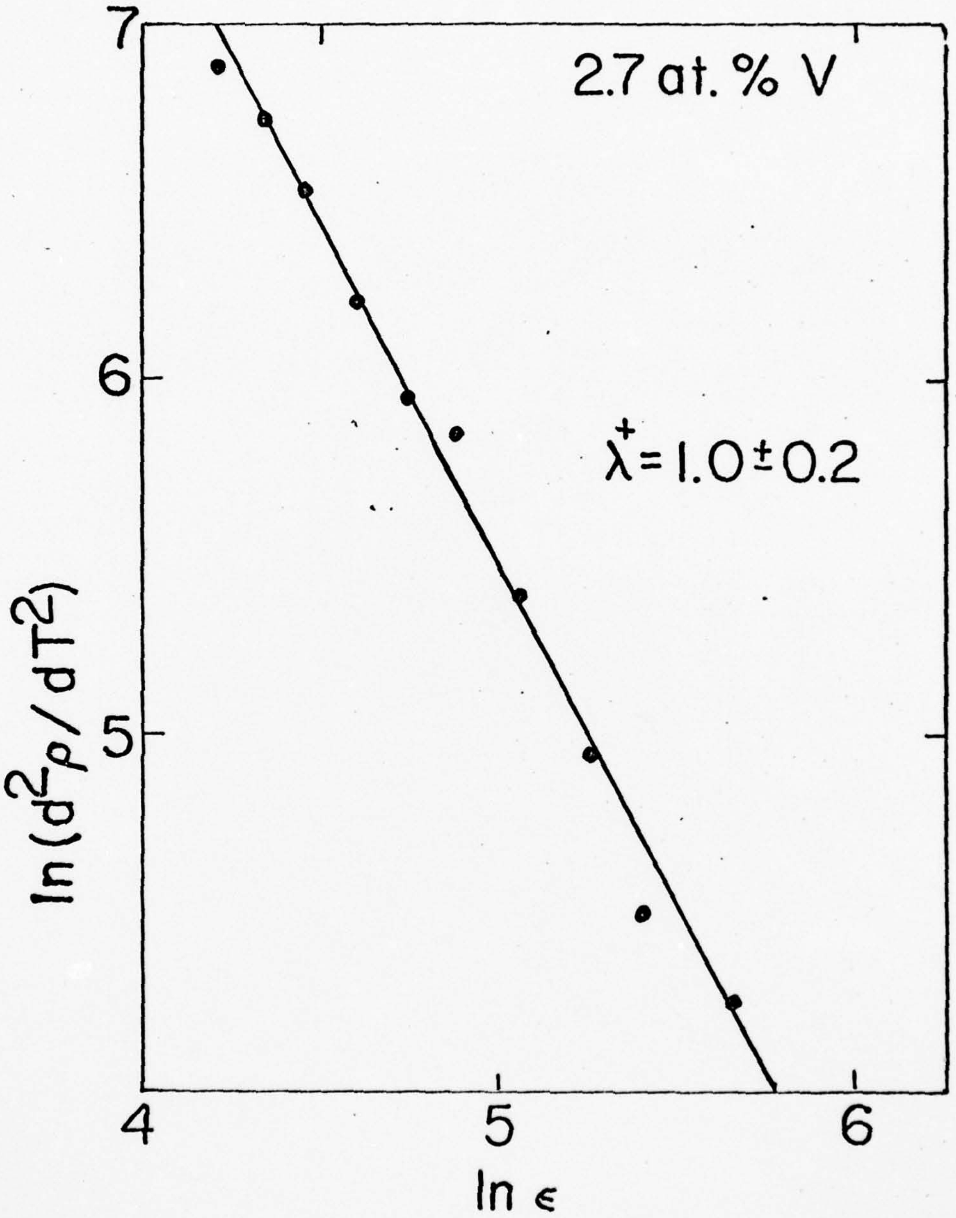


Fig. 6

Teoh et al

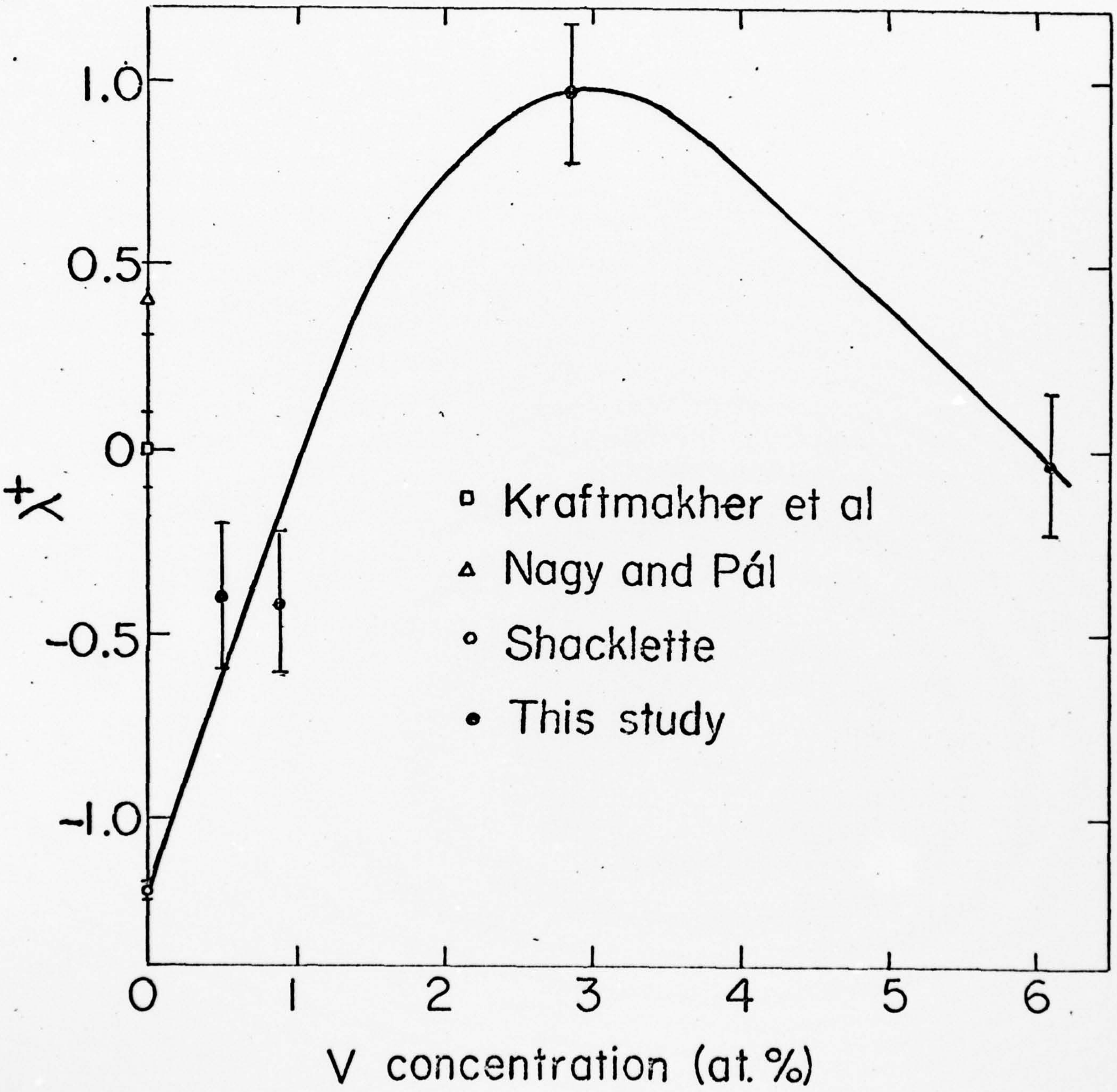


Fig. 7

Tech et al