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Determination of Curie Temperature, Short Range Order Parameter, and Number of Nearest Neighbors of Palladium Atoms to Iron Atoms in Palladium-Iron Alloys by Resistivity Measurement

YEN-CHANG WU (吳炎昌), J. CHEN (陳卓)
and SHENG-HENG FANG (方聲恒)

Department of Physics, National Taiwan University

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This article describes the measurement of resistivity of Pd-Fe alloys (8.82, 11.23, 13.22 15.00. and 17.87 atomic percent Fe) under temperatures from 77 °K to 400°K, each alloy having quenched, and quenched and aged states. The alloys have their Curie temperature T_c in each state found from their resistivity vs. temperature curves, together with short-range order parameter α_1. It is found that T_c is higher in aged samples.

The curves of alloys (excluding the 1787 at % Fe sample) are calculated for ρ_m, the resistivity due to magnetic scattering. At $T>T_c$, ρ_m is a constant, in close agreement with the expariment of Mydosh, and also the theory of Sivertsen on the resistivity of ferromagnetic alloys. With increase of atomic percentage of Fe (or decrease of that of Pd), the effect of aging decreases, This is similar to Sato's result of measuring the specific heat of Cu-Pd alloys.

INTRODUCTION

IN 1958, Hansen[1] drew the phase diagram of Pd-Fe alloys, and pointed out that at higher temperatures, no matter what are the atomic percentages of Pd and Fe, the continuous region of solid solution all has face-centered cubic lattice structure. At lower temperatures, with atomic percentage of iron between 0 and 60%, the face centered cubic lattice structure is still stable. In the same year, Gestenberg[2] measured the magnetic susceptibility of Pd-Fe alloys containing 1, 3, 5, 7 atomic percent of Fe, and pointed out that even when the iron atomic percentage is as low as 1 at %, the alloy will be still strongly magnetic. Crangle[3,4] in 1960 and 1965, measured the magnetic susceptibility of Pd-Fe solid solution containing only 0.15 at % of Fe, and pointed out that the strongly magnetic nature of the alloy is not due solely to Fe atoms. A part is due to the magnetic moment produced by Pd atoms. His suggestion raised the interest

(1) M. Hansen: *Constitution of Binary Alloys.* 2nd edition p. 697 (McGraw-Hill Book Co. Inc., N. Y. 1958).
(2) D. Gestenberg: Ann. Phys. 2, 236 (1958).
(3) J. Crangle: Phil. Mag. 5, 335 (1960).
(4) J. Crangle and W. R. Scott: J. Appl. Phys. 36, 921 (1965).

of many workers toward the study of Pd-Fe alloys, those related to resistivity measurements[5-8] being given as follows :

In 1969, Williams and Loram[5] measured the resistivity of Pd-Fe alloys containing 0.16-0.78 at % Fe. The sample was quenched, and the resistivity measured by standard four-probe method, with temperature range of 0.5-77 °K. The kink occured in the resistivity vs. temperature curve was taken as Curie temperature. In 1970, Mydosh et *al.*[8] measured the resistivity of Pd-Fe alloy with 12 at % Fe, the sample being quenched and aged, in a temperature range of 4.2-300°K, and the temperature corresponding to the maximum value of derivative of the resistivity vs. temperature curve was taken as Curie temperature.

The present article describes a measurement of the resistivity of Pd-Fe samples, either quenched from 950 °C (abbreviated Q) or quenched from 950 °C and then aged for two weeks at 325°C[9] (abbreviated A), measurement being done using van der Pauw method[10] through a temperature range of 77-400°K, taking the kink of resistivity vs. temperature curve as Curie temperature.

Samples treated through Q or A are aimed at a change of atomic arrangement of Pd and Fe in alloys, so as to study the change of properties of Pd and Fe at different atomic arrangement conditions.

THE EXPERIMENT

Samples were prepared with 99.98% pure Fe and 99.99% pure Pd. Both were first cut into chips of suitable size, washed with acetone, and weighed. They were then mixed in desired proportion, put into a quartz tube, and inserted into a vacuum high frequency induction furnace. The assembly was then pumped to a vacuum of about 10^{-3} mmHg and argon gas was then passed in to make the pressure inside the quartz tube to be about 0.2-0.4 kg/cm^2 above atmospheric pressure. The furnace was then started and melting was done under around 1,600°C. Ten minutes after melting, the furnace was shut down and the sample cooled down to room temperature inside the furnace under the same atmosphere and then withdrawn. Melting was repeated three times in the same way to assure homogeneity of composition and the sample was then transferred to a siliconite electric resistance furnace, where it was heated at 950 °C in argon atmosphere for one week for further homogenization, and then cooled in furnace to room temperature under the same atmosphere.

(5) G. Williams and J. W. Loram: J. Phys. Chem. Solids. 30, 1827 (1969).
(6) J. A. Mydosh et al.: J. Appl. Phys. 40, 1202 (1969).
(7) J. A. Mydosh et *al:* Phys. Rev. (B) 2, 1587 (1950).
(8) J. A. Mydosh et *al.*: Phys. Rev. (B) 2, 3613 (1970).
(9) Sheng-Heng Fang: Chinese J. Phys. 9, 9 (1971).
(10) L. J. van der Pauw: Philip. Res. Repts. 13, 334 (1958).

The sample was then rooled into slabs of about 2 mm thickness in a slab mill, with intermediate annealings in vacuum or in argon atmosphere for restoring ductility. Finally it was rolled into film of 0.08 mm in a film mill.

A small piece was cut from the alloy film, heated in vacuum for half an hour at 950 °C and then quenched in silicon oil. This is quenched sample, designated by Q. The quenched sample was further heated at 325 °C in vacuum for two weeks in an automatically temperature controlled electric resistance furnace to make the aged sample, designated by A. For resistivity measurement, the sample was cut into clover-leaf shape as shown in Fig. 1. Conduction leads were spot-welded onto the four connecting points. Resistivity measurements were done by van der Pauw method. The electric circuit used is shown in Fig. 2. Five alloy compositions were used, and an example of the measured resistivity vs. temperature curves is plotted in Fig. 3.

Using the kinks of the curves as Curie temperatures, T_c, our results are assembled in the following Table 1

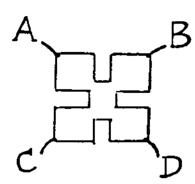

Fig 1

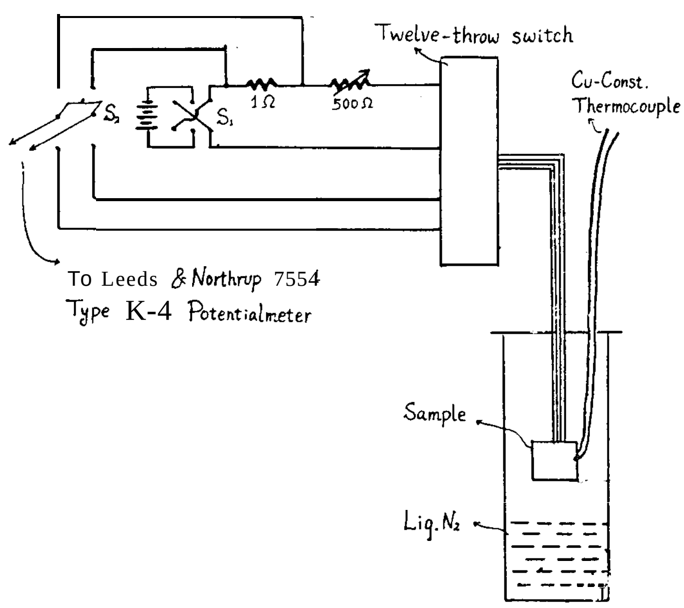

Fig. 2

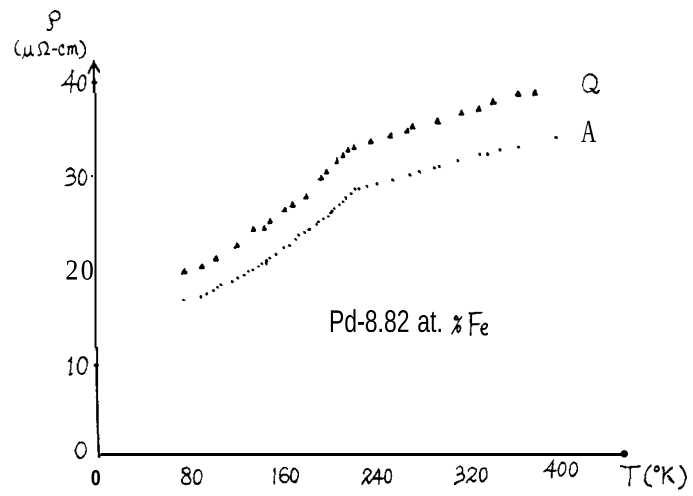

Fig. 3

Table 1

Alloy number	Composition	State	T_c (quenched)	T_c (quenched and aged)	α_1	Z
1	Pd-8.82 at % Fe	Q A	215°K	222°K	0.060 0.066	10.285 10.241
2	Pd-13.22 at % Fe	Q A	260°K	267°K	0.069 0.074	9.917 9.864
3	Pd-13.22 at % Fe	Q A	303°K	310°K	0.080 0.086	9.581 9.518
4	Pd-15.00 at % Fe	Q A	346°K	353°K	0.095 0.100	9.231 9.180
5	Pd -17.87 at % Fe	Q A	404°K	410°K	0.110 0.115	8.769 8.720

COMPARISON OF CURIE TEMPERATURE

The measured Curie temperatures in the present experiment, together with those measured by Crangle[3,4] from magnetic susceptibility, those measured by G. Longworth et ab.[11] from electrical resistivity, those measured by Williams[5] from electrical resistivity (sample quenched from 1,130°C) and those measured by Mydosh *et al.*[6,7,8] from electrical resistivity (sample with 0.25 at % Fe, quenched from 1,100°C) are given in Fig. 4.

A note is to be given here regarding the expressions for short range order parameter α_1 and the number of palladium atoms nearest to iron atoms Z:

$$\alpha_1 = 1 - \frac{1}{X_A}\left(1 - \frac{T_c}{1,500}\right)$$

and

$$Z = 12X_A(1 - \alpha_1),$$

where X_A is the molar fraction of palladium atoms.

(11) G. Longworth and C. C. Tsuei: Phys. Letters **27A**, 258 (1968).

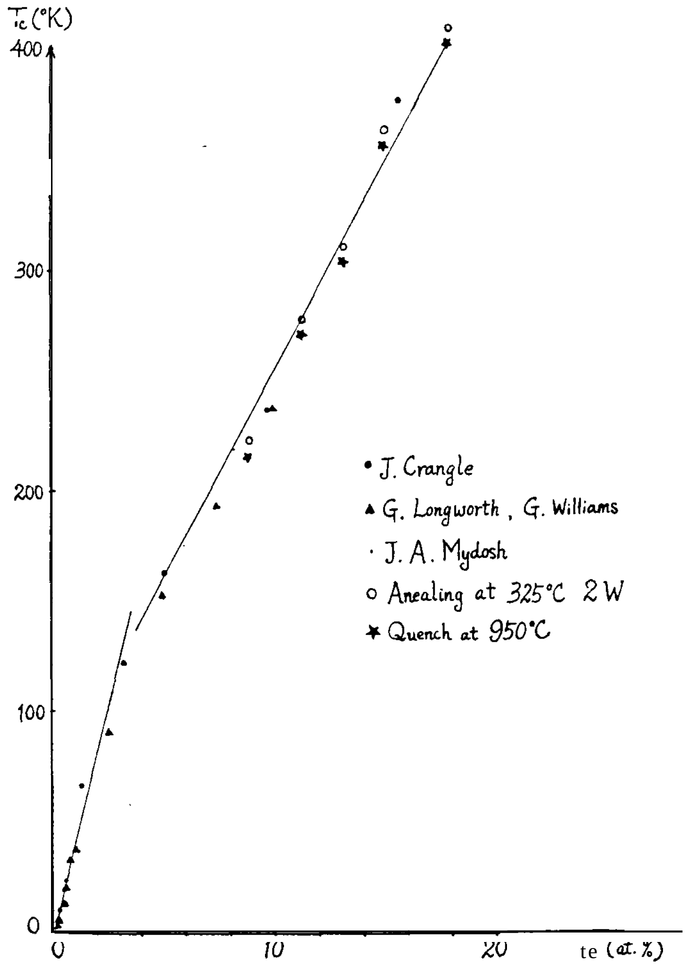

Fig. 4

COMPARISON OF QUENCHED AND AGED SAMPLES

1. We can see from the above Table that samples after aging treatment will have Curie temperatures higher compared with the corresponding quenched samples. This shows that aging treatment will promote the magnetic behavior of alloys.
2. Short range order parameter α_1 are all greater than zero[(12)], in other words, the alloys are all in clustering state. The values of α_1 for aged samples are all greater than those for the corresponding quenched samples. This shows that aging treatment tends more toward clustering phenomenon.
3. The number of palladium atoms nearest to the iron atoms Z will be smaller for a samples compared with that for the corresponding quenched samples. This shows that aging treatment will draw palladium atoms closer to the iron atoms.

(12) Y. Sato et al.: Phys. Rev. **B1**, 1402 (1970).

COMPARISON WITH THEORY

According to Coles[13], electrical resistivity can be written approximately as

$$\rho = \rho_m + \rho_{th} + \rho_0$$

where ρ_m is the part of resistivity due to magnetic scattering, ρ_{th} is the part of resistivity due to phonon interaction, and ρ_0 is the part of resistivity independent of temperature. Sivertsen in 1964[14] published a theory that ρ_m tends to be a constant for temperatures above T_c. This agrees with Mydosh's experimental result[6,7,8]. ρ_m is proportional to T^2 at low temperatures. But Sivertsen assumed a dilute alloy to begin with. Yet we found that the qualitative feature still remain the same even for samples with Fe as high as 15 atomic percent.

CONCLUSIONS

1. At temperatures above the Curie temperature, magnetic scattering resistivity maintains a fixed value in the present experiment. This agrees with the experimental result of Mydosh and the theory of Sivertsen.
2. When the short range order parameter α_1 increases, the resistivity decreases and at the same time the Curie temperature increases. This agrees with the theory of Sivertsen.
3. Aging of the sample causes increase of short range order parameter α_1, or aging will increase the magnetic susceptibility of the sample.
4. When in an alloy the percentage of Fe increases, the effect of aging decreases. This is similar to the result of measuring the specific heat of Cu-Pd alloys by Sato[12].
5. The experimental result confirms at least qualitatively Sivertsen's theory for ρ_m.

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(13) B. R. Coles: Adv. in Phys. 7 40 (1958).
(14) J. M. Sivertsen: J. Appl. Phys. 35, 2407 (1964).