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PARAMAGNETISM OF POLYCRYSTALLINE NICKEL

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Abstract—Because of appreciable discrepancies among past experimental studies of the paramagnetic behavior of nickel at elevated temperatures, we have carefully measured the magnetic susceptibility of two high purity nickel samples up to 1500°K. These measurements are in reasonable agreement with Fallot's (1944) studies. Phenomenologically, between 740 and 970°K the magnetic susceptibility follows the Curie–Weiss law, $\chi = C/(T-\theta_p)$, with $C = 5{\cdot}54_6 \times 10^{-3}$ cm^3 °K g^{-1} and $\theta_p = 654{\cdot}1$°K. At higher temperatures deviation from this law occurs which is describable by an additional temperature dependent contribution to the total susceptibility.

INTRODUCTION

RECENTLY we have started to investigate the magnetic properties of binary nickel-rich alloys in order to increase our knowledge of the origin of magnetism in transition metals. For the analysis of the alloying effects, one has to have reliable information on the magnetic behavior of pure nickel. One property of interest is the paramagnetic susceptibility. Although this quantity for nickel has been studied extensively in the past, we have found that available data not only show considerable scattering but also are mutually quite inconsistent, especially at elevated temperatures. Thus it was decided to review this problem and to measure carefully the magnetic susceptibility of nickel as a function of temperature above its ferromagnetic Curie point. The experimental results of this investigation are described in this paper.

EXPERIMENTAL CONSIDERATIONS

Two nickel samples (designated by 1 and 2) were used in this experiment. Sample 1 was made from high purity nickel by means of levitation melting.* The analysis of this metal, provided by the supplier, is given in Table 1. It was found that during the levitation melting considerable gas evolution occurred. Metallographic examination also revealed that this metal contained sizable amounts of inclusions. Therefore, it was necessary to purify this nickel by melting it together with about 0·02% carbon in a zirconia crucible. This procedure gave metal from which small levitation melts (dia. $\frac{3}{8}$ in., length $\frac{3}{4}$ in.) were easily made. Metallographic examination after the carbon treatment showed practically no inclusions present. The ratio $\rho(4{\cdot}2)/\rho(298)$, where $\rho(4{\cdot}2)$ and $\rho(298)$ are the electrical resistivities at 4·2 and 298°K, respectively, was found to be $3{\cdot}3 \times 10^{-3}$ for the purified nickel.

Table 1. *Partial analysis of nickel* (*sample* 1)

Impurities	Amount [p.p.m.]
Fe	10
Al	7
Si	5
Ca	2
Cu	2
Mg	2
Ag	< 1
Mn	< 1
As,Au,B,Ba,Be,Bi,Cd,Co, Cr,Cs,Ga,Ge,Hf,Hg,In,Ir, K,Li,Mo,Na,Nb,Os,P,Pb,Pt, Rb,Re,Rh,Ru,Sb,Se,Sn,Sr, Ta,Ti,Tl,V,W,Zn,Zr	Not detected

* Obtained from Johnson–Mathey Co.

This quantity is a reasonable value for high purity nickel.[1]

Sample 2 was prepared from electrolytic nickel.* A partial list of impurities according to the supplier is presented in Table 2. This nickel was

Table 2. Partial analysis of nickel (sample 2)

Impurities	Amount [w/o]
Fe	0·01
Cu	0·01
C	Trace
Co	Trace
S	Trace
Si	Trace

melted in a vacuum of about 10^{-4} mm Hg using a magnesium oxide crucible and then was cast in a copper mold (dia. $\frac{1}{2}$ in., length $6\frac{1}{2}$ in.). The ratio of the electrical resistivity at 4·2 and 300°K of this material was found to be $33{\cdot}7 \times 10^{-3}$. The same nickel has been used to make nickel-rich nickel–niobium alloys whose electrical resistivities have been studied earlier.[2]

The nickel samples, whose susceptibilities were measured, were enclosed in silica capsules evacuated to 10^{-5} mm Hg. The magnetic susceptibility was determined with the Faraday method using essentially the apparatus described before[3] except for some improvements. The most important of them is the addition of a controller maintaining a stability of 1 part in 10^4 in the electric current in the solenoid. Another improvement is the replacement of the Mettler Type B–5 balance by a Sartorius Series 2500 semi-micro-balance capable of detecting weight changes of 0·01 mg. Third, a program controller, by means of which the furnace temperature can be varied in a predetermined manner, has been added.

The diamagnetic corrections of the quartz capsules, determined experimentally, were applied to the data to obtain the total magnetic susceptibilities of the nickel samples.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows in a conventional manner the measured inverse magnetic susceptibility per gram ($1/\chi$) of both nickel samples as a function of the absolute temperature (T). The susceptibility values were found to be independent of the magnetic field. The data clearly indicate that the susceptibilities of samples 1 and 2 are the same. Furthermore, we also found no hysteresis effects, i.e., the susceptibility of the samples at a particular temperature was independent of the previous thermal history.

Figure 1 also presents the susceptibility of most of the earlier studies[4–8] for which the numerical data have been published. The inconsistency of the various results especially at elevated temperatures and the scattering of the points are quite noticeable. Of all the above-mentioned studies our data agree in the most satisfactory way with the measurements of FALLOT.[8] The magnetic susceptibility of polycrystalline nickel has also been determined recently by NAKAGAWA.[9] Although he does not give numerical susceptibility data (and thus the comparison with our results is difficult) it appears from his $1/\chi$ vs. T plot that his results at high temperatures are somewhere between TERRY's[6] and those of SUCKSMITH and PEARCE.[7]

It is obvious from Figure 1 that the magnetic susceptibility of nickel does not obey the Curie–Weiss law

$$\chi = \frac{C}{T-\theta_p} \tag{1}$$

over the whole temperature range. The quantities C and θ are the Curie constant and the paramagnetic Curie temperature, respectively. However, according to our data, the Curie–Weiss law is phenomenologically applicable in the temperature range from about 740 to 970°K. Using the method of least squares we obtained from the susceptibility data on the sample 1 the quantities C and θ_p to be $5{\cdot}54_6 \times 10^{-3}$ cm^3 °K g^{-1} and 654·1°K, respectively. This value of C gives the paramagnetic moment of a nickel atom $\mu_p = 1{\cdot}61_3$ Bohr magnetons. The above-given values were obtained from the measured magnetic susceptibility data without correcting for the diamagnetism of nickel. This quantity is believed to be small and difficult to estimate exactly. FALLOT[8] quotes it to be $-0{\cdot}00307 \times 10^{-6}$ g^{-1} cm^3. For these reasons we, as usually done by other investigators, neglect this small contribution in our analysis of the data.

* Obtained from Williams and Co.

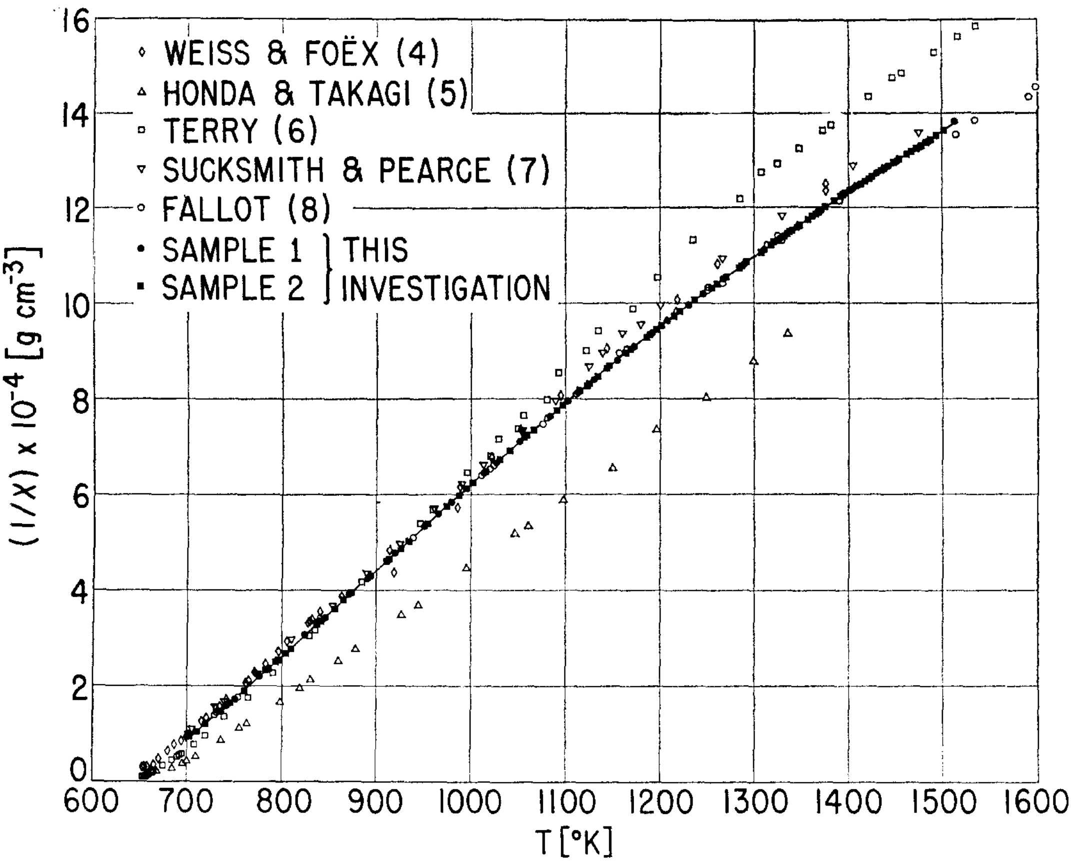

FIG. 1. Inverse magnetic susceptibility of nickel as a function of temperature.

The downward curvature in the $1/\chi$ vs. T plot of nickel at high temperature indicates a contribution to the susceptibility in addition to the Curie–Weiss term. It seems quite generally accepted[8, 10, 11] that the paramagnetic behavior of nickel and many nickel binary alloys can be represented by the equation

$$\chi = \frac{C}{T-\theta_p}+\chi_a, \tag{2}$$

where χ_a is assumed to be independent of the temperature. Several values of χ_a for nickel have been given in the literature.[8, 11, 12] Since χ_a has a possible theoretical meaning (paramagnetic susceptibility of s-electrons, orbital contribution of d-electrons, influence of s–d exchange interactions, effect of s–d transfer)[13–16] a more accurate knowledge of it is of some importance. Our attempts to obtain χ_a completely independent of the temperature have been unsuccessful. That is, we found it impossible to fit our susceptibility data to equation (2) with χ_a as a constant over the whole temperature range.

Since it is convenient phenomenologically to use equation (2) for describing the magnetic susceptibility, we decided to consider χ_a as a function of temperature. This quantity is shown in Fig. 2. The points were obtained from the measured magnetic susceptibility values on the sample 1 using our values of C and θ as given above.

Finally, it may be remarked that we also tried to fit our experimental data to the equation

$$\chi = \alpha+\beta T+\gamma/T \tag{3}$$

which has been used by KAUFMANN and STARR[17] for certain nickel–copper alloys. This, too, was found to be impossible.

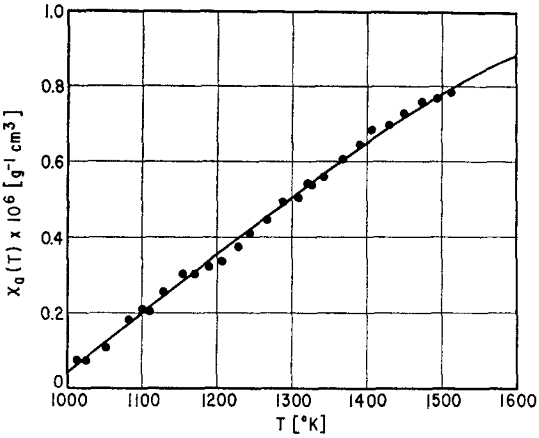

FIG. 2. χ_a of nickel (sample 1) as a function of temperature.

Recently it has been suggested by KOCH and ARROTT,[18] and by DANIELIAN[19] that it is more advantageous to plot $1/\chi T$ vs. $1/T$ instead of $1/\chi$ vs. T for analyzing the susceptibility data. This plot is particularly useful for obtaining the Curie constant and the interaction parameters based on the localized electron model. Figure 3 shows the magnetic susceptibility data of the sample 1 as the graph of $1/\chi T$ vs. $1/T$. The open points in this figure were calculted from FALLOTT's measurements,[8] made up to about 100°K above the melting point (m.p.) of nickel, in order to extend our plot at high temperatures. Moreover, it appears that even then one cannot reliably extrapolate the quantity $1/\chi T$ for $1/T = 0$ primarily because of the scattering of Fallot's points. An attempt was made to plot $1/(\chi-\chi_a)T$ vs. $1/T$ using various χ_a values. It was not possible to obtain a straight line, demonstrating, as already mentioned above, that the paramagnetic susceptibility of nickel does not follow equation (2).

Finally, it should be remarked that in spite of recent theoretical and experimental advances toward the understanding of the electronic structures of the transition elements[20, 21] no completely satisfactory theories of the paramagnetic behavior of the ferromagnetic transition metals exist at the present time.

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REFERENCES

1. WHITE G. K. and WOODS S. B., *Phil. Trans. Roy. Soc.* **251**, 273 (1959).
2. ARAJS S., *J. appl. Phys.* **32**, 97 (1961).

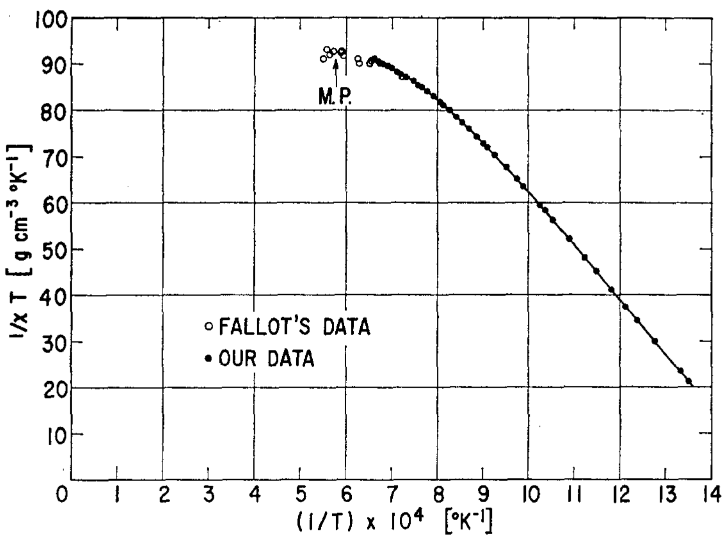

FIG. 3. Koch–Arrott–Danielian plot for nickel (sample 1).

3. ARAJS S. and MILLER D. S., *J. appl. Phys.* **31,** 986 (1960).
4. WEISS P. and FOËX C., *Arch. Sci. Natl.* **31,** 89 (1911).
5. HONDA K. and TAKAGI H., *Sci. Rep. Tohoku Univ.* **1,** 229 (1911).
6. TERRY E. M., *Phys. Rev.* **9,** 394 (1917).
7. SUCKSMITH W. and PEARCE R. R., *Proc. Roy. Soc.* **A167,** 189 (1938).
8. FALLOT M., *J. phys. Radium* **5,** 153 (1944).
9. NAKAGAWA Y., *J. phys. Soc. Japan* **11,** 855 (1956).
10. NÉEL L., *Ann. phys.* **5,** 232 (1936).
11. VOLKOV D. I. and CHECHERNIKOV V. I., *Izv. akad. nauk. S.S.S.R.* **21,** 1099 (1957).
12. OWE BERG T. G., *J. phys. Radium* **12,** 418 (1951).
13. SHIMIZU M., *J. phys. Soc. Japan* **16,** 1114 (1961).
14. KUBO R. and OBATA Y., *J. phys. Soc. Japan* **11,** 547 (1956).
15. VLASOV K. B. and VONSOVSKII S. V., *Fiz. met. metall.* **2,** 403 (1956).
16. WOHLFARTH E. P., *Proc. Roy. Soc.* **A195,** 434 (1949).
17. KAUFMANN A. R. and STARR C., *Phys. Rev.* **63,** 445 (1943).
18. KOCH F. B. and ARROTT A., *Bull. Amer. phys. Soc.* **7,** 263 (1962).
19. DANIELIAN A., *Proc. phys. Soc. Lond.* **80,** 981 (1962).
20. HERRING C., *J. appl. Phys.* **31,** 35 (1960).
21. BROOKS H., *Electronic Structure and Alloy Chemistry of the Transition Elements*, p. 3 (edited by BECK P. A.) Interscience, New York (1963).