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EFFECT OF PRESSURE ON THE MAGNETIC PROPERTIES OF NICKEL AND NICKEL ALLOYS

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I hereby recommend that this dissertation prepared under my direction by Edmond G. Michigan entitled Effect of Pressure on the Magnetic Properties of Nickel and Nickel Alloys be accepted as fulfilling the dissertation requirement of the degree of PhD

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*This approval and acceptance is contingent on the candidate's adequate performance and defense of this dissertation at the final oral examination. The inclusion of this sheet bound into the library copy of the dissertation is evidence of satisfactory performance at the final examination.

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SIGNED: Edmond C. McClizan

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ABSTRACT

The resistivity of nickel and 20 and 30 atomic percent Cu-Ni alloys has been measured at hydrostatic pressures up to 7 kbar. The Curie temperature in nickel was found to vary as $+0.35 \pm 0.003°K/kbar$ and in Ni-Cu alloys as $+0.15 \pm 0.01°K/kbar$ for 20 at% and $+0.07 \pm 0.02°K/kbar$ for 30 at% alloys, respectively. The resistivity of palladium has also been measured at high pressures for comparison with the resistivity of nickel in order to obtain an estimate of the dependence of the saturation magnetization of nickel at 0°K on pressure. The exchange integral J is shown to vary as r^{-n}, where r is the lattice parameter, and $n = 6.9 \pm 1.2$. By the rigid band approximation the ratio of the shift in s-d overlap to the fractional change in the lattice parameter is estimated at 7.8 eV.

I. INTRODUCTION

Experiments to determine the influence of hydrostatic pressure on the Curie temperature, T_c, and the spontaneous magnetization, σ, of ferromagnetic metals and alloys have been carried out actively in recent years. Such experiments enable one to determine the functional dependence of exchange interaction on inter-atomic distance. As Kouvel and Wilson[1] point out, for a tight-binding description, a variation of the saturation magnetic moment with pressure is related to a change in the spin-aligning force within a single atom, while a change of the Curie point with pressure is due primarily to the change in the inter-atomic exchange forces.

Patrick[2] used the a.c. transformer method and estimated the rate of change of Curie temperature with pressure (dT_c/dP) by observing the parallel shift of the secondary voltage *versus* temperature curve in the neighborhood of the steepest descent of the curve. Fujiwara *et al.*,[3] by measuring the change in the saturation flux, measured the rate of change of magnetization with pressure ($d\sigma/dP$) and also determined dT_c/dP by extrapolating σ^2 near the Curie temperature for various pressures. By using the differential extraction method, Bloch and Pauthenet[4] measured the magnetization, and, by observing the weak field permeability, determined the Curie temperature as a function of pressure by extrapolation.

It should be noted that the determination of T_c through measurements of quantities such as magnetization, weak field permeability, etc. does not necessarily insure reproducible results with good accuracy especially in the experimental conditions involving pressure application. These properties are easily affected by the previous handling of the specimen, depend partly on the local potential at which Bloch walls are located and inherently require the presence of magnetic fields for their measurement. In addition the procedure of extrapolation for the determination of the Curie point is ambiguous because of the presence of a pronounced magnetic order in the neighborhood of the ferromagnetic Curie point.

The resistivity anomaly below ferromagnetic transition, for instance, in nickel has been known since the measurement of Holborn,[5] Gerlach,[6] and Potter.[7] The advantage of the resistance measurement in the determination of the Curie point is that it does not require a measuring magnetic field and that the resistance change is partly attributable to band structure change that takes place in the ferro- to paramagnetic transition.[8] Thus the ferromagnetic origin of the resistance change is independent of the domain walls, i.e., magnetization process and is likely to possess good reproducibility. It is also possible to obtain relative values of magnetization from the resistivity measurement especially for nickel where the band description is considered adequate.[9]

Thus it appears that significant information can be obtained by employing the resistivity measurement in studying the magnetic properties of ferromagnetic materials, especially nickel, at high pressures. In addition, similar study on nickel-copper alloys at high pressures should yield supplementary information on the band description of nickel as the classic experiment at atmospheric pressure did earlier.[10] Results of the measurement on the effect of pressure on the resistivity _versus_ temperature characteristics of pure nickel, pure palladium and nickel-copper alloys of 20 and 30 atomic percent are reported here.

II. EXPERIMENTAL PROCEDURE

A. Preparation of Specimens

Nickel and palladium of 99.999% purity were obtained from United Mineral and Chemical Corporation in ¼mm diameter wire form. Two alloys were prepared using high purity copper (99.999%) and nickel (99.99%). These alloy compositions were in atomic percent: 20 Cu-80 Ni, and 30 Cu-70 Ni. They were vacuum melted by induction heating and the ingots were drawn into 0.25mm wires by the standard method. Final copper content of these two alloys was determined chemically and found to be: 19.70 and 29.62 atomic percent, respectively.

B. Apparatus and General Procedure

The pressure system used in this experiment was a modified Bridgman-type liquid system described elsewhere.[11] Dow Corning 200 silicone fluid (3 centistokes) was used as the pressure medium. The pressure was measured with a coil of manganin wire calibrated against the freezing point of mercury at 0°C (7490 bar). The uncertainty in the pressure measurements was less than ± 1%.

The pressure vessel was machined from Carpenter 883 steel and hardened to Rockwell 40C. The available sample space was 12mm in diameter and 19mm long. Thermocouple and potentiometric probes for the sample were led out from the vessel through chromel, alumel, and steel cones seated in the pressure plug and insulated by unfired lava A (American Lava Corporation).

The pressure vessel was mounted inside an air furnace. Two thermocouples located along the specimen indicated that the temperature gradient along the entire length of the sample was less than ± .15°C. The specimen wire was insulated with a fibre-glass tubing and wound around the thermocouples.

The electric resistivity was measured by the standard d.c. potentiometric techniques. Resistivity measurement was carried out with a heating rate of 3 - 10°C per hour while the pressure was held constant.

III. RESULTS

Figures 1 and 2 show the relative electrical resistivities of 99.999% pure nickel and 99.999% pure palladium, respectively, as a function of temperature for pressures of 1 bar, 2, 5, and 7 kbar. Here the relative resistivity was taken as ρ/ρ_0, where ρ and ρ_0 are observed values of resistivity at T°C and at 32°C, respectively. Figure 3 shows the detail of the relative resistivities of nickel and Figures 4 and 5 that of the two alloys (20%Cu-80%Ni and 30%Cu-70%Ni) for small temperature ranges near their respective Curie temperatures.

IV. DISCUSSION

A. Determination of T_c

The onset of ferromagnetism can be clearly seen as a sudden change in the curvature of ρ/ρ_0 *versus* T plots in Figures 3, 4, and 5. The point of intersection of the two portions of the resistivity plot--the segment immediately above T_c and that below T_c--can be determined either graphically or through least-squares curve fitting to a high degree of reproducibility for repeated measurements. The Curie point thus determined was reproducible to better than ± 0.03°C for pure nickel and the alloys. The Curie temperature thus determined is plotted against pressure in Figure 6.

The linear dependence of Curie temperatures on pressure is evident in these plots. The slopes of these plots, dT_c/dP, as well as T_c, are shown in Table 1. It is to be noted that the present result on the pressure dependence of T_c agrees well with Patrick's[2] values which are 0.35°C/kbar for nickel and 0.07°C/kbar for 30%Cu-70%Ni alloy. Results of Bloch and Pauthenet[4] are 0.32, 0.14 and 0.05°C/kbar, respectively, for Ni, 20%Cu-80%Ni, and 30%Cu-70%Ni.

The pressure coefficient of T_c for pure nickel was obtained by plotting ℓnT_c *versus* pressure and its slope measured to be $(5.53 \pm 0.02) \times 10^{-7}$ per bar. All straight lines were fitted by the least squares method.

B. Determination of σ_0

The saturation magnetization of Ni as a function of temperature at various pressures can be obtained by comparison of ρ/ρ_0 versus T curves of Ni and Pd at corresponding pressures as analyzed earlier for one atmospheric pressure.[7,12] Based on the simple two-band model Mott[9] described the ferromagnetic resistivity drop as due to the decrease in the density of states of the final state in the s-d scattering of electrons below T_c. By assuming that the top of the d-band for nickel is parabolic, he showed that the average resistivity is

$$\rho = \rho_{ss} + \tfrac{1}{2}\rho_{sd}\left\{\left(1 - \frac{\sigma}{\sigma_0}\right)^{1/3} + \left(1 + \frac{\sigma}{\sigma_0}\right)^{1/3}\right\} \qquad (1)$$

where σ is the spontaneous magnetization at T°K and σ_0 is the saturation magnetization at 0°K, while ρ_{ss} and ρ_{sd} are resistivities due to phonon induced s-s and s-d transitions, respectively.

By setting $\sigma = 0$ in Eq. (1) one obtains the average resistivity for a hypothetical non-ferromagnetic nickel to be labeled henceforth as ρ^*.

$$\rho^* = \rho_{ss} + \rho_{sd} \cdot \tag{2}$$

For $(\sigma/\sigma_o) << 1$, Eq. (1) reduces to

$$\begin{aligned} \rho &= \rho_{ss} + \rho_{sd} - \frac{1}{9}\rho_{sd}\left(\frac{\sigma}{\sigma_o}\right)^2 \\ \rho &= \rho^* - \frac{1}{9}\rho_{sd}\left(\frac{\sigma}{\sigma_o}\right)^2 . \end{aligned} \tag{3}$$

Electronically Pd and Ni are similar. They both have incomplete d-shells, but the number of holes/atom are somewhat different. Shimizu[13] by theoretically analyzing the temperature dependence of the paramagnetic susceptibility of Pd estimated the number of holes in the d shell of Pd to be approximately 0.32 holes/atom. More recently, Vuillemin[14] performed a de Haas van Alphen effect experiment for palladium and his measurements yield the value of 0.36 holes/atom in Pd. The susceptibility of Pd decreases linearly with increasing concentration of H and its paramagnetism is suppressed at about 55% H which with the assumption of the rigid band model will imply that Pd has about 0.55 holes/atom in its d shell.[15] The number of holes/atom in Ni has been estimated to be 0.1 holes/atom in the s shell and 0.5 holes/atom in the d shell.[16] Ni and Pd being similar, except for a scale factor we set $\rho^* = \rho_{Pd}$ and Eq. (3) is rewritten

$$\frac{\Delta\rho}{\rho_0} = \frac{1}{\rho_0}(\rho_{Ni} - \rho_{Pd}) = -\frac{1}{9}\left(\frac{\sigma}{\sigma_0}\right)^2 . \tag{4}$$

Values of $\Delta\rho/\rho_0$ are read from graphs similar to that of Fig. 7, except that the coefficient 1/9 in Eq. (4) was to be replaced by 0.47 to agree with zero kilobar experimental data.[17] Experimentally then, the values of σ/σ_0 can be determined. One can determine σ_0 from these values by adjusting the parameter of the Brillouin function. Thus the value of σ_0 was obtained for each pressure. The pressure coefficient of σ_0 was calculated to be $(-3.4 \pm 0.4) \times 10^{-7}$ per bar.

In Fig. 8 the intercept is interpreted as the effective number of Bohr magnetons per atom of pure nickel. In Fig. 9 four intercepts, one corresponding to each pressure, is a measure of the effect of pressure on the saturation moment of pure nickel.[18] Although from the present data the intercepts are in the neighborhood of 63%, which is higher than the accepted value of 60%,[6,19] one can nevertheless determine the pressure coefficient of the saturation magnetization σ_0, namely $(1/\sigma_0)(d\sigma_0/dP)$, where σ_0 is given by

$$\sigma_0 = ng\mu_B S . \tag{5}$$

In Eq. (5), n is the number of atoms per unit mass, g is the g factor, μ_B is the Bohr magneton, and S is the average spin moment per atom. It follows that

$$(1/\sigma_0)(d\sigma_0/dP) = (1/S)(dS/dP) \ . \tag{6}$$

$g\mu_B S$ for a given pressure is the intercept determined from Fig. 8. When ℓnS is plotted versus pressure the slope is found to be $(-3.4 \pm 0.2) \times 10^{-7}$ per bar which is consistent with the value obtained from Mott's theory.

C. Determination of J as a Function of Inter-Atomic Distance and the Shift in Relative s-d Overlap with Pressure

According to the simple molecular theory, a connection between the exchange energy J and the Curie temperature T_c is given by

$$T_c = \frac{2zJ\ S(S+1)}{3k} \ . \tag{7}$$

In the classical limit $S(S+1)$ is replaced by S^2 and by using Eq. (5) one obtains

$$T_c \sim J\ \sigma_0^2 \ , \tag{8}$$

and it then follows that

$$(1/J)(dJ/dP) = \left[(1/T_c)(dT_c/dP)\right] - \left[(2/\sigma_0)(d\sigma_0/dP)\right] \ . \tag{9}$$

All quantities on the right side of Eq. (9) have been estimated from experimental measurements as outlined above. The left hand side was calculated to yield

$$(1/J)(dJ/dP) = (12.33 \pm 0.40) \times 10^{-7} \text{ per bar}$$
$$= -\kappa \, d(\ell nJ)/d(\ell nV) \; , \qquad (10)$$

where κ, the compressibility of nickel, was taken as 5.35×10^{-7} per bar.[20] From Eq. (10) it follows that J has r^{-n} dependence where r is the inter-atomic distance and $n = 6.9 \pm 1.2$.

An elementary calculation based on the rigid band model, the saturation moments as read from Fig. 8, and the assumption that the bottom of the 4s band and the top of the 3d band of nickel are parabolic yields

$$\Gamma = (9.4 \pm 0.7) \times 10^{-3} \text{ eV} \; ,$$

where Γ is the shift in the relative s-d overlap for 7 kbar. For 7 kbar the fractional change in the lattice parameter for nickel is

$$\frac{\Delta r}{r} \simeq 1.2 \times 10^{-3} \; ,$$

and the ratio of these two quantities is

$$[\Gamma/(\Delta r/r)] = \frac{9.4}{1.2} = 7.8 \text{ eV} \; .$$

V. CONCLUSIONS

In this paper we have taken up the effect of pressure on the Curie temperature by observing the anomalies in the resistance *versus* temperature curves for each pressure and for each alloy. The dependence of saturation moment on pressure was obtained by two methods. One method was plotting Curie point *versus* copper concentration for various pressures, while the other method was based on Eq. (4) which connected resistivity to magnetization and made use of the Brillouin function.

With the pressure coefficients of T_c and σ_0, we estimated $(1/J)(dJ/dP) = 12.33 \times 10^{-7}$ per bar which in turn gave $J \sim r^{-8.9}$.

TABLE 1.

	Ni	20%Cu-80%Ni	30%Cu-70%Ni
T_c	630.6°K	433.0°K	330.5°K
dT_c/dP	0.35 ± .003 °K/kbar	0.15 ± .01 °K/kbar	0.07 ± .02 °K/kbar

TABLE 2.

Pure Nickel

	0 kb	2 kb	5 kb	7 kb
n_+ No. of Holes	0.6320	0.6315	0.6308	0.6303

$$\frac{1}{\sigma_o}\frac{d\sigma_o}{dP} = (-\ 3.4 \pm .4) \times 10^{-4}/\text{kbar}$$

Figure 1. The relative electrical resistivity of nickel as a function of temperature and pressure.

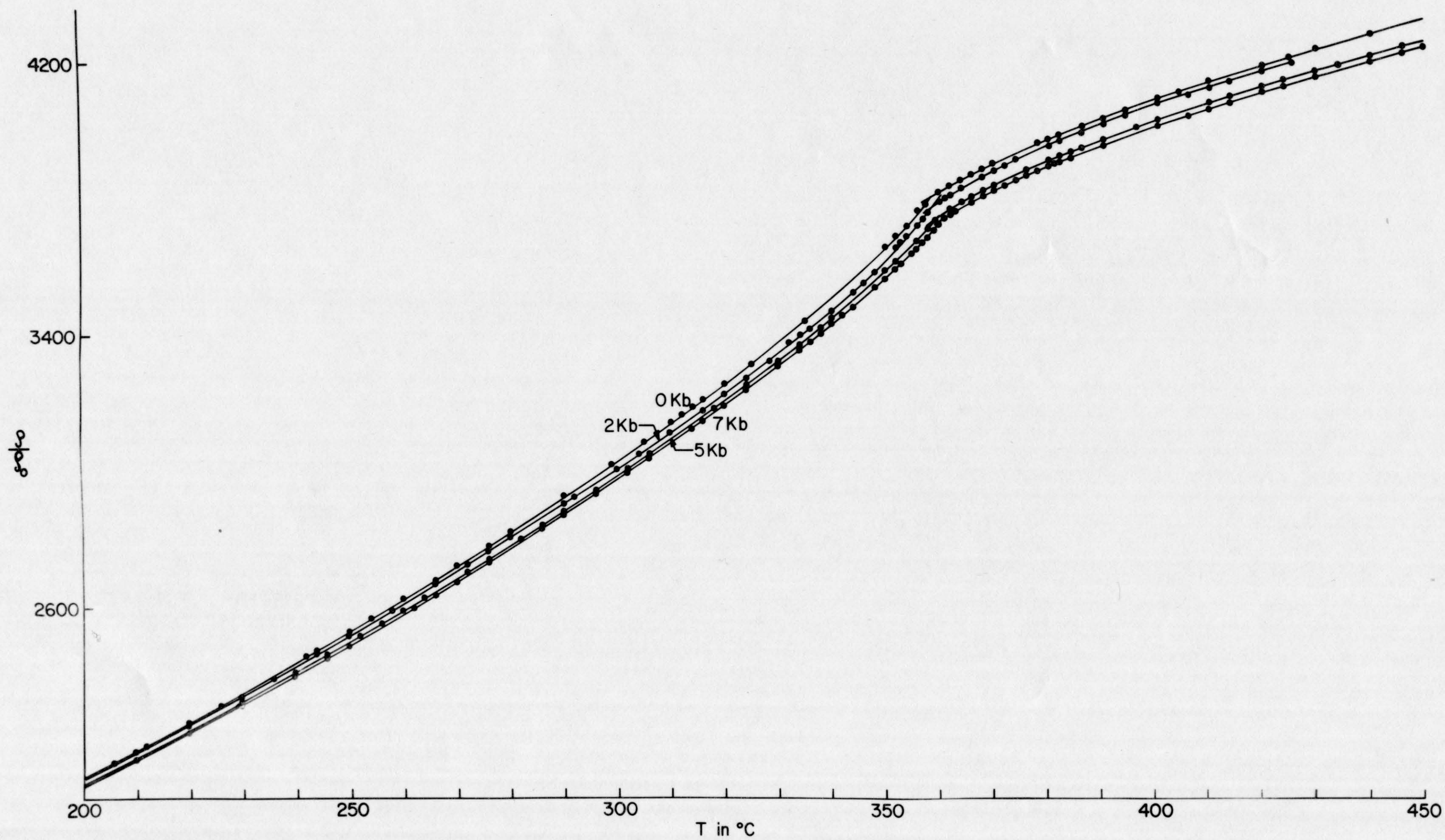

4200
3400
2600
ρ/ρ_0
0 Kb
2 Kb
7 Kb
5 Kb
200
250
300
350
400
450
T in °C

Figure 2. The relative electrical resistivity of palladium as a function of temperature and pressure.

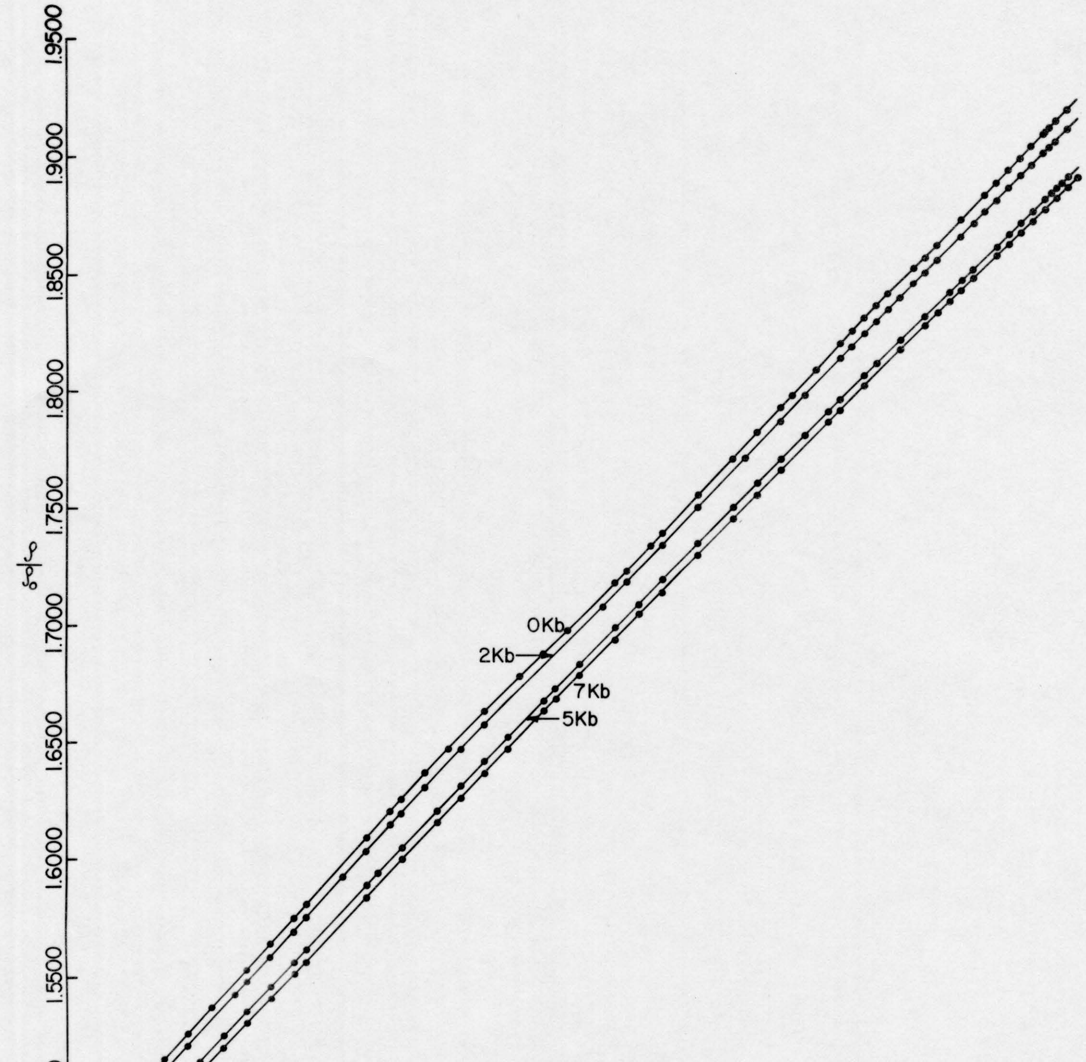
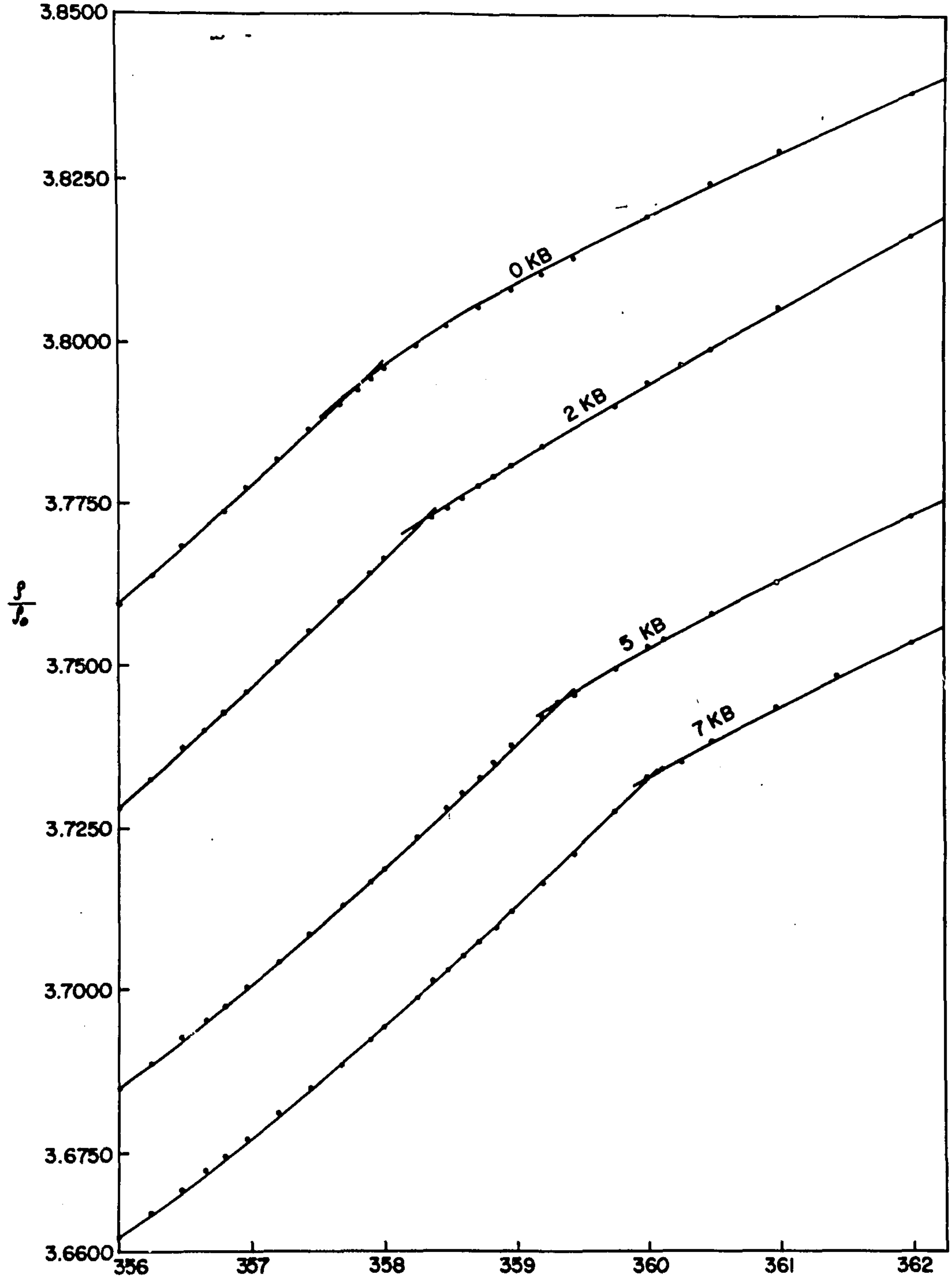

1.9500
1.9000
1.8500
1.8000
1.7500
1.7000
1.6500
1.6000
1.5500
1.5000
1.4500
200
250
300
350
T in °C
0Kb
2Kb
7Kb
5Kb

Figure 3. The relative electrical resistivity of nickel as a function of temperature and pressure in the neighborhood of T_c.



3.8500
3.8250
3.8000
3.7750
3.7500
3.7250
3.7000
3.6750
3.6600
$\frac{\rho}{\rho_0}$
0 KB
2 KB
5 KB
7 KB
356
357
358
359
360
361
362

Figure 4. The relative electrical resistivity of 20%Cu-80% Ni alloy as a function of temperature and pressure in the neighborhood of T_c.

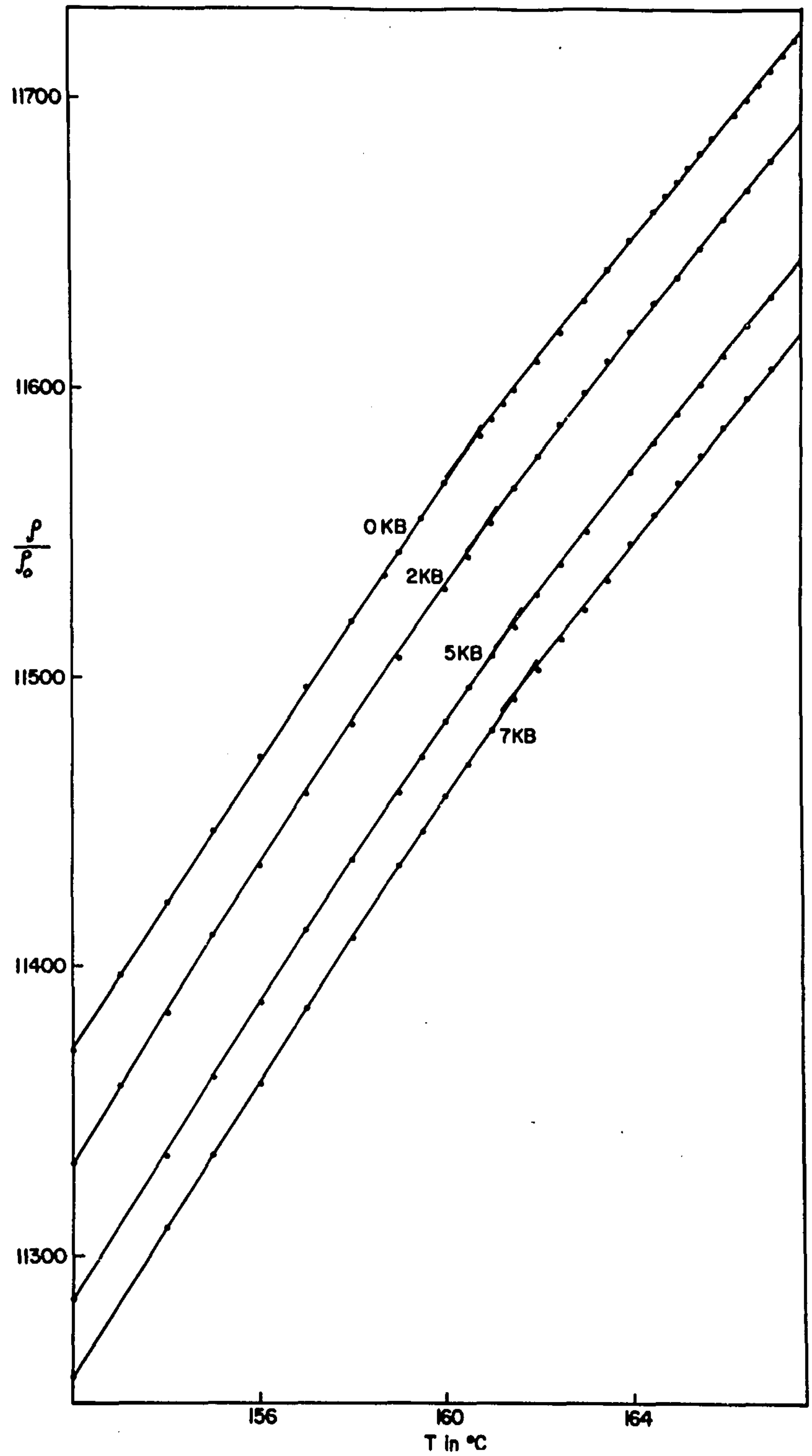
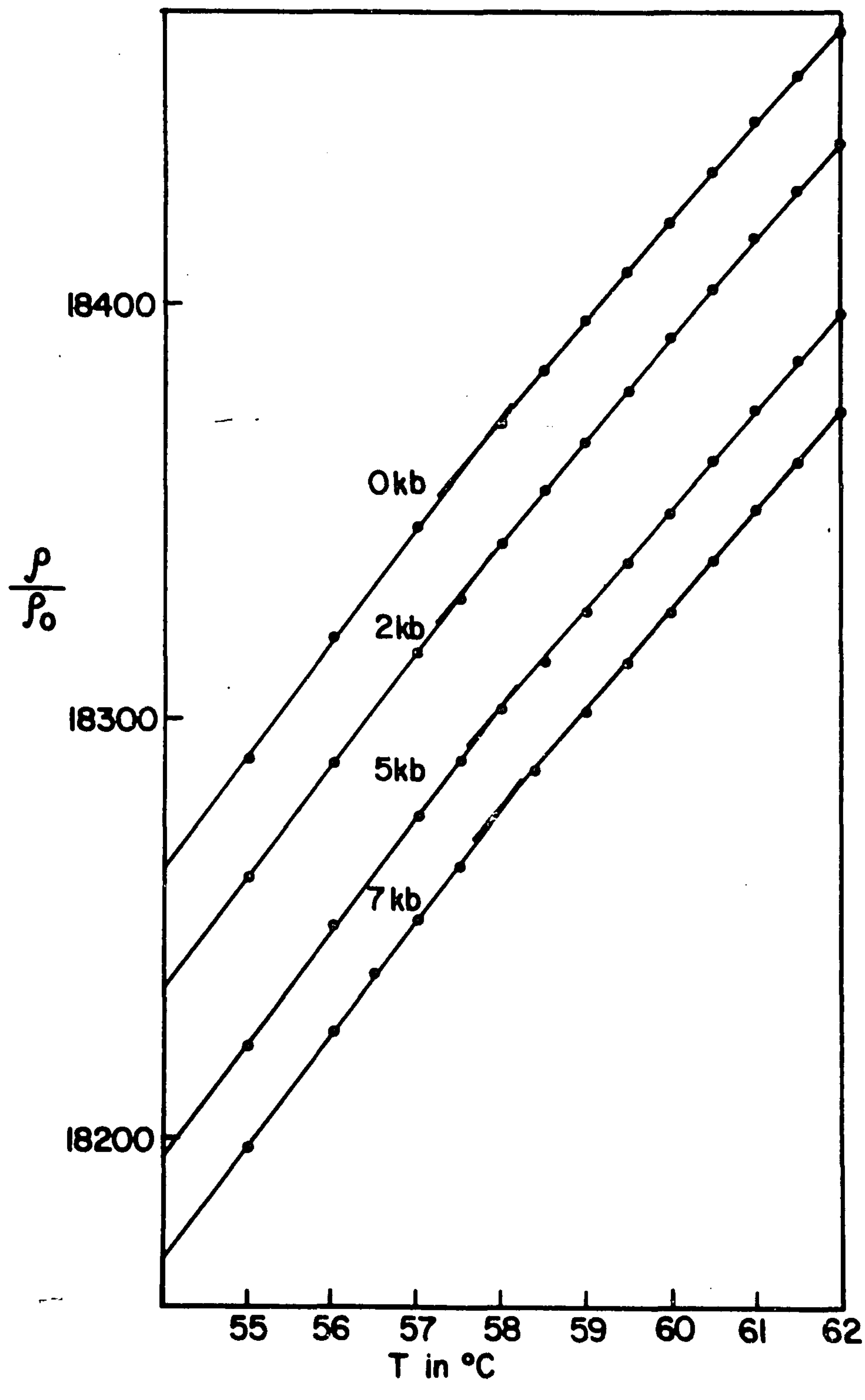

11700
11600
11500
11400
11300
$\frac{\rho}{\rho_0}$
0 KB
2KB
5KB
7KB
156
160
164
T in °C

Figure 5. The relative electrical resistivity of 30%Cu-70% Ni alloy as a function of temperature and pressure in the neighborhood of T_c.



18400
18300
18200
$\frac{\rho}{\rho_0}$
0kb
2kb
5kb
7kb
55
56
57
58
59
60
61
62
T in °C

Figure 6. Change of Curie point versus pressure.

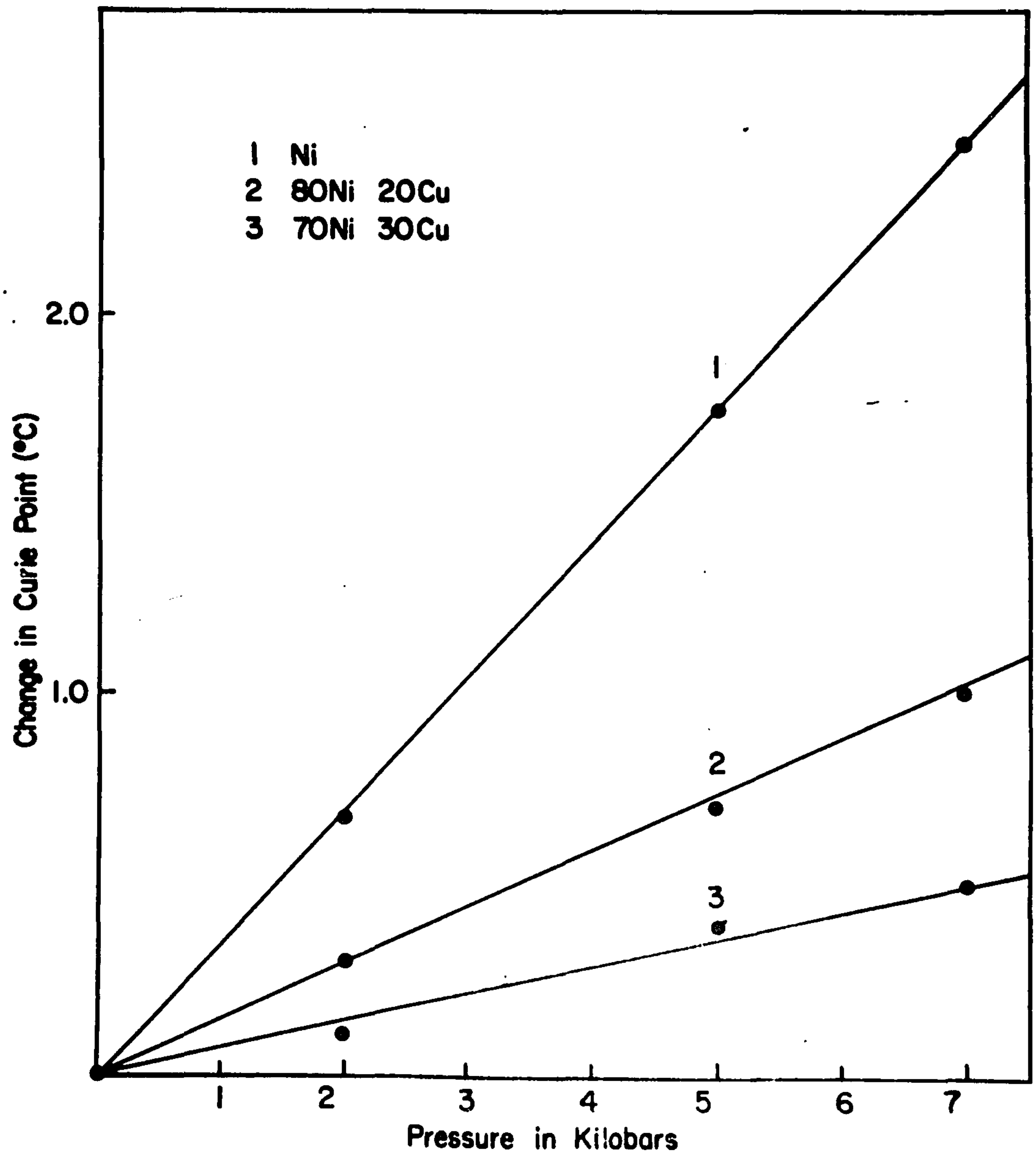
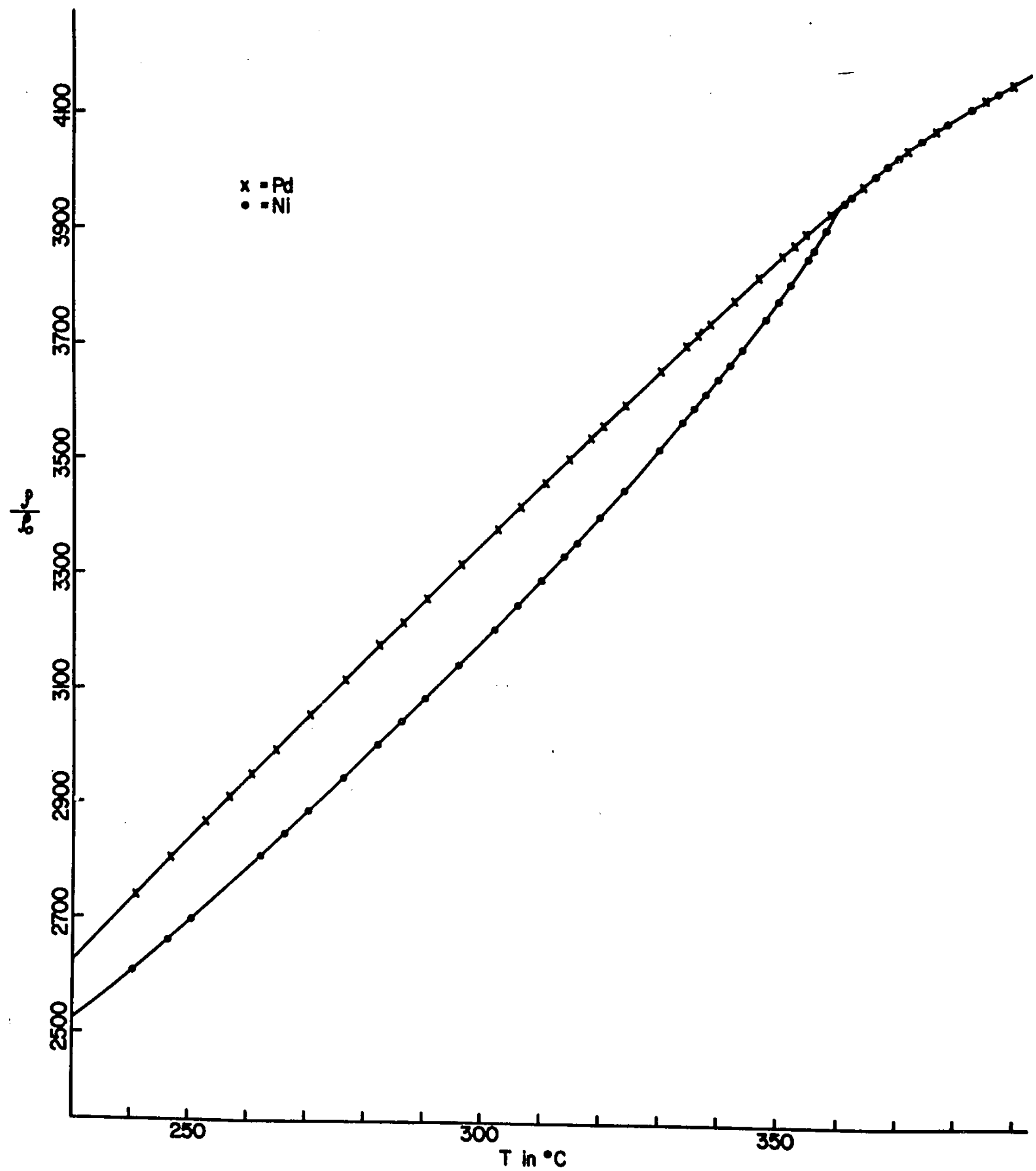
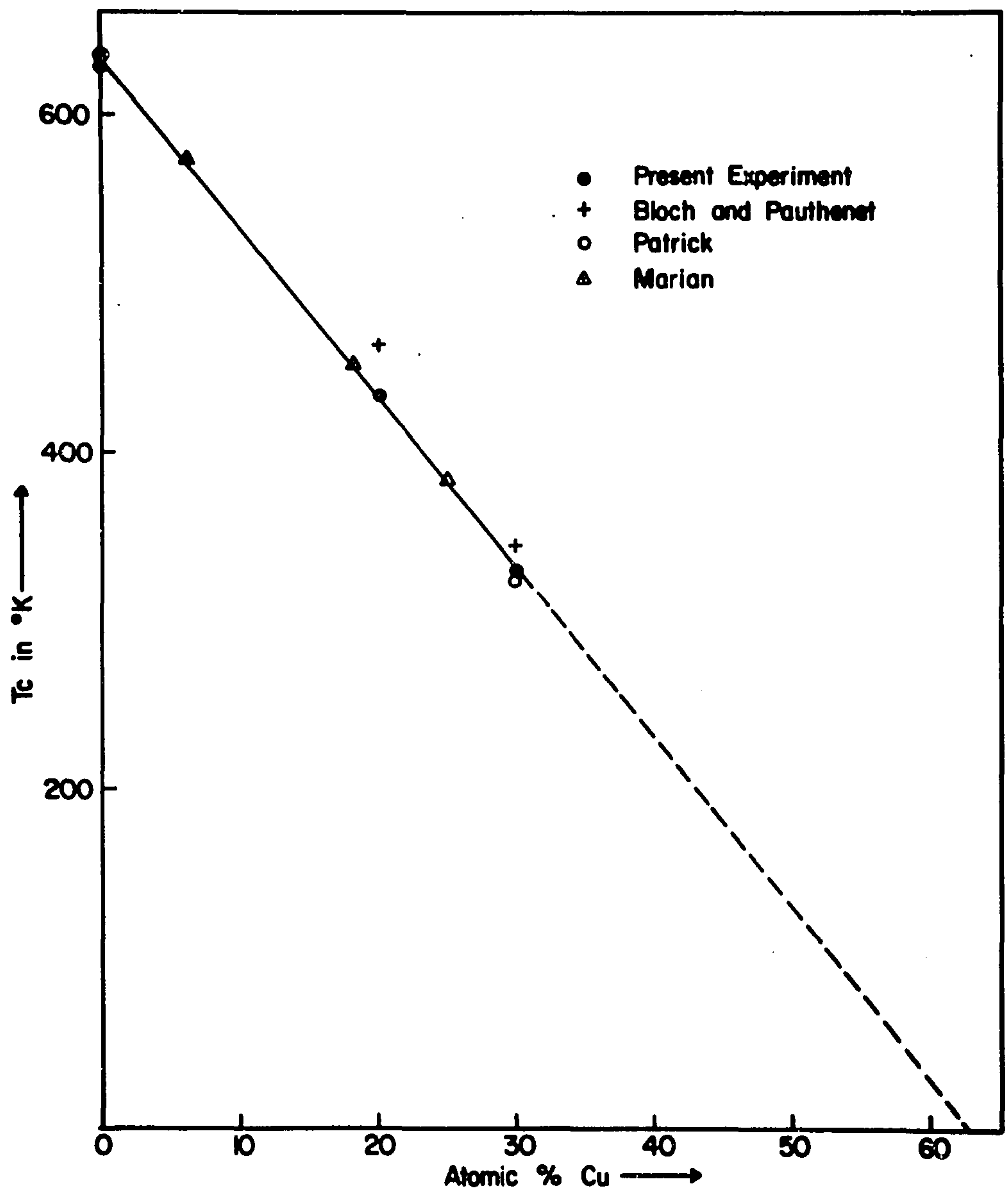

1 Ni
2 80Ni 20Cu
3 70Ni 30Cu
2.0
1.0
Change in Curie Point (°C)
1
2
3
1 2 3 4 5 6 7
Pressure in Kilobars

Figure 7. Compound plot of electrical resistivity of Ni and the normalized resistivity of Pd at 7 kbar.



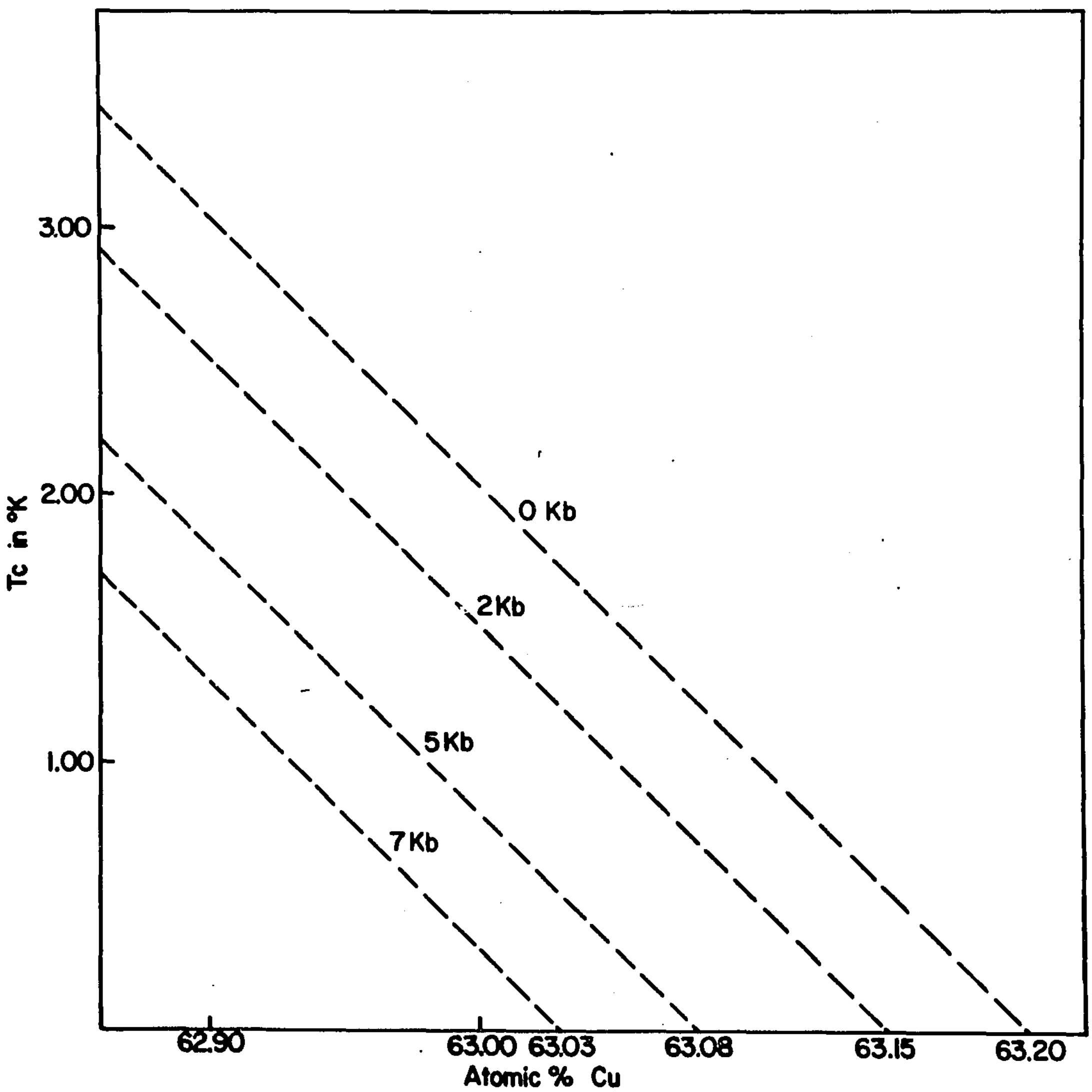
x = Pd
• = Ni
ρ/ρ₀
2500
2700
2900
3100
3300
3500
3700
3900
4100
250
300
350
T in °C

Figure 8. Change of Curie point versus copper concentration at atmospheric pressure.



600
400
200
Tc in °K
0
10
20
30
40
50
60
Atomic % Cu
Present Experiment
Bloch and Pauthenet
Patrick
Marian

Figure 9. Change of Curie point versus copper concentration as a function of pressure.


3.00
2.00
1.00
Tc in °K
O Kb
2Kb
5Kb
7Kb
62.90
63.00
63.03
63.08
63.15
63.20
Atomic % Cu

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