Reprinted from JOURNAL OF APPLIED PHYSICS, Vol. 36, No. 3 (Part 2), 1229–1231, March 1965

Printed in U. S. A.

1. Magnetic
Alloys

Magnetic Properties under Pressure of Some Transition Metal Alloys

D. BLOCH AND R. PAUTHENET
Laboratoire d'Electrostatique et de Physique du Métal, B.P. 319, Grenoble, France

We have studied the variation of the Curie temperature θ_f and the spontaneous magnetization σ_s of several transition metals and some of their solid solutions as a function of the pressure. The measurements were carried out between 77° and 700°K. In the system Ni–Si, $d\theta_f/dp$ varies from 0.32×10^{-3} °K bar^{-1} for pure nickel to 0.05×10^{-3} °K bar^{-1} for Ni–9 at.% Si. The magnitude of $d\theta_f/dp$ decreases by 0.033×10^{-3} °K bar^{-1} per 1% of Si dissolved. In the system Ni–Cu, $d\theta_f/dp$ decreases by 0.01×10^{-3} °K bar^{-1} per 1% of Cu dissolved. For polycrystalline cobalt, $(\sigma_l)^{-1}(\partial\sigma_l/\partial p)$, at 293°K, is equal to $-10\pm1.5\times10^{-7}$ bar^{-1}. The molecular field coefficient, representing the exchange integrals, increases for a decrease in volume in the case of Fe, Ni, Co, and the solid solutions Ni–Si, Ni–Cu, Fe–Si. The relative variation of the spontaneous magnetization with pressure is accounted for by the use of band theory.

THE study of ordered magnetic states presents in particular two fundamental problems; one is related to the spontaneous magnetic moment and the other to the coupling forces between the moments. The theoretical and experimental study of the variation of the magnetization and the exchange integral with interatomic distance in the transition metals and their solid solutions is difficult to carry out, but it may be very important to the understanding of their magnetic properties.

APPARATUS

By compressing petroleum ether or gaseous helium in a high-pressure multiplier,[1,2] pressures p varying regularly up to 10 000 bars can be obtained in a useful volume of 6 cm^3. The experimental chambers are made of nonmagnetic copper alloy containing 2% beryllium. The Curie temperatures θ_f were determined by observing the temperature variation of the weak field permeability for a given pressure. The ferromagnetic magnetization was measured using a differential extraction method, extraction from the center of the electromagnet airgap of the specimen under pressure, in a magnetic field which can be varied from 0 to 30 000 Oe.

EXPERIMENTAL RESULTS

The Curie point has been defined as being the temperature at which the tangent at the inflection point of the curve plotting the variation of the susceptibility cuts the temperature axis. At atmospheric pressures, the observed values (Table I, Fig. 1) are in good agreement with previous determinations.[3] At 293°K, the magnetization of cobalt in a field of 29 000 Oe can be considered as being near the value of the spontaneous magnetization σ_s, and that as a result the pressure variation of the magnetization at 29 000 Oe represents approximately the corresponding variation of the spontaneous magnetization. For polycrystalline cobalt, $(\sigma_s)^{-1}(\partial\sigma_s/\partial p)=-10\pm1.5\times10^{-7}$ bar^{-1}, at 293°K. In the three previous low-field reported measurements on cobalt, values of about -13.5,[4] -1.5,[5] and -2.2[6] were obtained.

It is possible to determine the value of $(\sigma_0)^{-1}(\partial\sigma_0/\partial p)$, at a given temperature T, using[2]:

$$\sigma_0^{-1}\left(\frac{\partial\sigma_0}{\partial p}\right)_T=\sigma_s^{-1}\left(\frac{\partial\sigma_s}{\partial p}\right)_T+\sigma_s^{-1}\left(\frac{\partial\sigma_s}{\partial T}\right)_p\frac{T}{\theta_f}\left(\frac{\partial\theta_f}{\partial p}\right)_T. \quad (1)$$

For iron, cobalt, and the iron–silicon alloys the second term of the second member, where $T<300$°K, is negligible.[7] For cobalt, $(\sigma_0)^{-1}(\partial\sigma_0/\partial p)=-10\pm1.5\times10^{-7}$ bar^{-1}, at 293°K. For iron we have taken the mean value[5,8,9] $(\sigma_s)^{-1}(\partial\sigma_s/\partial p)=-4\times10^{-7}$ bar^{-1}; $(\sigma_0)^{-1}\times(\partial\sigma_0/\partial p)$ is noticed to be independent of temperature; $(\sigma_0)^{-1}(\partial\sigma_0/\partial p)=-4\times10^{-7}$ bar^{-1}. For nickel it has been experimentally shown[5,10,11] that $(\sigma_s)^{-1}(\partial\sigma_s/\partial p)$ is in the order of -2×10^{-7} bar^{-1} at 293°K and -2.9×10^{-7}

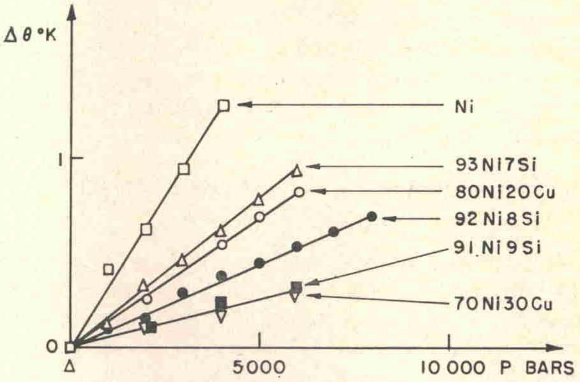

FIG. 1. Curie temperature θ_f as a function of pressure.

---

[1] D. Bloch and R. Pauthenet, Compt. Rend. **254,** 1222 (1962).
[2] D. Bloch and R. Pauthenet, Proc. Intern. Conf. on Magnetism, Nottingham, 1964 (to be published).
[3] V. Marian, Ann. Phys. (Paris) **7,** 459 (1937).
[4] D. Gugan, Proc. Phys. Soc. (London) **72,** 1013 (1958).
[5] E. Tatsumoto, H. Fujiwara, H. Tange, and T. Hiraoka, J. Phys. Soc. Japan **17,** 592 (1962); **18,** 1348 (1963).
[6] J. S. Kouvel and C. C. Hartelius, J. Appl. Phys. **35,** 940 (1964).
[7] L. Patrick, Phys. Rev. **93,** 384 (1954).
[8] R. Gersdorf, Thèse, Amsterdam (1961).
[9] F. Galperine, S. Larine, and A. Shishkov, Dokl. Akad. Nauk SSSR **89,** 419 (1953).
[10] A. Ebert and A. Kussmann, Physik. Z. **38,** 437 (1937).
[11] J. S. Kouvel and R. H. Wilson, J. Appl. Phys. **32,** 435 (1961).

TABLE I. Curie points and their pressure dependence for nickel and several alloys.

	Ni	93 Ni 7 Si	92 Ni 8 Si	91 Ni 9 Si	80 Ni 20 Cu	70 Ni 30 Cu
θ_f°K	633.1	365.7	317.9	308.1	463.1	343.1
$(d\theta_f/dp)\,10^8 d°$ bar^{-1}	0.32±0.02	0.16±0.02	0.0915±0.02	0.05±0.04	0.14±0.02	0.05±0.02

bar^{-1} at 4.2°K [12]; as a result of (1) $(\sigma_0)^{-1}(\partial\sigma_0/\partial p)$ is constant and in the order of -2.8×10^{-7} bar^{-1} between 4.2° and 293°K. The same determinations can be carried out for the nickel or iron-base alloys (Table II). The saturation moment σ_0 is therefore dependent on the distance between carriers.

THE VARIATION OF THE MOLECULAR-FIELD COEFFICIENT WITH VOLUME

In a molecular field model, the molecular-field coefficient, n, representing the exchange integrals, varies as follows with the volume V:

$$\left(\frac{\partial\,\mathrm{Log}n}{\partial\,\mathrm{Log}V}\right)_T=\left(\frac{\partial\,\mathrm{Log}\theta_f}{\partial\,\mathrm{Log}V}\right)_T-2\left(\frac{\partial\,\mathrm{Log}\sigma_0}{\partial\,\mathrm{Log}V}\right)_T. \qquad (2)$$

Knowing the compressibilities,[13] one can deduce, from the experimental results (Table II), that $\partial\log n/\partial\log V$ is practically constant and in the order of -2 (Table II) for the elements studied. As a first approximation, n increases with decreasing interatomic distance d, proportionally as d^{-6}.

VARIATION OF SATURATION MOMENT WITH PRESSURE

The exchange interactions uncouple the electrons $3d$ in a half-band $3d\uparrow$ and a half-band $3d\downarrow$ [14–15]: nickel, possesses a complete half-band $3d\uparrow$ containing 5 electrons per atom, the half-band $3d\downarrow$ only contains about 4.4 electrons. Iron has two incomplete half-bands $3d\uparrow$ and $3d\downarrow$ containing respectively about 4.6 and 2.6 electrons per atom. Let us consider that the variation of magnetization with pressure is due, for nickel, to the transition of electrons from the conduction band to the half-band $3d\downarrow$, while for iron, it is caused by the transition of electrons from the $3d\uparrow$ half-band to the $3d\downarrow$ half-band, the number of conduction electrons staying practically constant. By studying the pressure variation of the resistance R of iron, cobalt, and nickel[16] and supposing the number of conduction electrons to remain constant, it has been shown that $\partial\log R/\partial\log V_{\mathrm{th}}$ must be equal to 4.3 for iron, 4.6 for nickel, and 4.7 for cobalt; values which are to be compared to the experimental values[13] of 4, 3.5, and 1.7; the difference between the theoretical and experimental values can be understood by considering that the greater part arises from the relative decrease in the number of conductions electrons on applying pressure.

The addition of small amounts of nonmagnetic materials, such as silicon or aluminium to iron decreases its magnetic moment by 2.2 μ_B. For each substituted atom,[17] the number of electrons in the half-bands $3d\uparrow$ and $3d\downarrow$ can vary, but the moment for iron remains constant, the density of states being the same at the top of the $3d\uparrow$ and $3d\downarrow$ half-bands. For Fe–Si solid solutions, $(\sigma_s)^{-1}(\partial\sigma_s/\partial p)$ is constant; this having already been observed for solid solutions of Fe–Al containing up to 22% aluminium.[18]

If one substitutes copper atoms for nickel atoms, the average number of electrons per nickel atom increases, which in turn reduces the population difference between

TABLE II. Volume dependence of the Curie point, the saturation moment, and the molecular-field coefficient for transition metals and alloys.

	Ni	90 Ni 10 Cu	80 Ni 20 Cu	70 Ni 30 Cu	51.6 Ni 48.4 Cu	Fe	96 Fe 4 Si	92.6 Fe 7.4 Si	89.4 Fe 10.6 Si
$\partial\log\theta_f/\partial\log V$	−0.95	−0.8*	−0.6	−0.25		0[a]	0.1[a]	0*	−0.2[a]
$\partial\log\sigma_0/\partial\log V$	0.5	0.6[b]	0.75[b]	0.95[b]	1.7[b]	0.7	0.8*	0.85[c]	0.87[c]
$\partial\log n/\partial\log V$	−1.95	−2	−2.1	−2.15		−1.4	−1.7	−1.7	−1.95

[a] See Ref. 7. [b] See Ref. 12. [c] See Ref. 8.

---

[12] E. I. Kondorsky and V. L. Sedov, Soviet Phys.—JETP **11,** 501 (1960).

[13] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. **81,** 169 (1952); **77,** 189 (1949).

[14] N. F. Mott, Proc. Phys. Soc. (London) **47,** 571 (1935).

[15] E. C. Stoner, Proc. Roy. Soc. (London) **A154,** 656 (1936).

[16] A. W. Lawson, Progr. Metal Phys. **6,** 1 (1956).

[17] M. Fallot, Ann. Phys. (Paris) **6,** 305 (1936).

[18] R. C. Hall, J. Appl. Phys. **28,** 707 (1957).

the two half-bands d which is responsible for the magnetic moment. Flechter[19] has calculated the form of the curve giving, for nickel, the density N of possible electronic states as a function of their energy E. On filling progressively the $3d\downarrow$ half-band for nickel, the energy difference, ΔE, between the top of the $3d\uparrow$ and $3d\downarrow$ bands decreases rapidly; the term $\partial\log\sigma_0/\partial\log V$ increases rapidly (Table II). For the iron-base alloys, ΔE and $\partial\log\sigma_0/\partial\log V$ are constant. From the curve $N(E)$ we can deduce that the product $\Delta E\partial\log\sigma_0/\partial\log V$ remains constant too for nickel base alloys.

The rigid-band approximation explains certain magnetic properties of the transition metals and their solid solutions under hydrostatic pressure up to 10 000 bars. It has been experimentally verified that the variation of magnetization with pressure is inversely proportional to the energy difference between the half-bands $3d\uparrow$ and $3d\downarrow$.

---

[19] G. C. Fletcher, Proc. Phys. Soc. (London) **65**, 192 (1952).