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Pressure Effect on the Curie Temperatures of Transition Metals and Alloys

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We determined the variation of the Curie temperature with pressure for iron, cobalt, nickel, six iron-nickel alloys, and five cobalt-nickel alloys. A permeability method in zero magnetic field has been used in a belt-type apparatus at pressures up to 90 kbar and temperatures up to 1400 °K. The pressure shifts measured for the Curie temperatures of iron and cobalt are zero; for nickel it is positive and markedly nonlinear. The Curie temperatures of face-centered-cubic iron-nickel alloys decrease very rapidly with pressure when the nickel content is low and show a progressively smaller decrease when nickel is added. They begin to increase when the nickel concentration is over 68 wt%. The existence of maxima on the curves of the Curie temperatures versus pressure or volume seems to be definitely established. Pressure increases the Curie temperature of cobalt-nickel alloys in all cases, but here also in a nonlinear way. For strong ferromagnets with a few carriers a band theory has been previously developed. The shift of the Curie temperature is then given by $d\theta/dP = \frac{5}{3}k\theta$ (k = compressibility). For pure nickel and nickel-cobalt alloys with a cobalt content less than about 50 wt% good agreement with experiment is obtained at low pressures, but not at higher pressures. The Curie temperature shift of Invar-type alloys has been previously calculated using a weak-itinerant-electron-ferromagnet band theory. In this case we have been able to predict and observe a parabolic decrease of the Curie temperature with pressure: $\theta^2 = \theta_0^2\,(1 - P/P_0)$. In order to explain the shifts for the different fcc alloys of nickel with iron, use is made of a model where γ-iron is supposed to have two electronic levels and which gives account of many properties of these alloys at normal pressure.

I. INTRODUCTION

Many of the properties of ferromagnets can be explained through the introduction of a molecular field which can be justified by a spin Hamiltonian. The magnetic properties are then supposed to arise from electrons which are well localized on particular atoms. Thus it is possible to explain many features of ionic compounds, but not to describe the properties of $3d$ transition metals for which it can be shown that magnetism is not due to localized electrons, but rather to free, or at least partly free, electrons, since they play some role in the electrical conductivity. Band ferromagnetism has then been developed to account for this property.

In order to obtain a better understanding of ferromagnetism in these $3d$ transition metals and their alloys we have undertaken a study of the effect of pressure on the Curie temperature, which is one of the essential features of ferromagnets.

Application of pressure to a ferromagnet, whether this is a metal or an insulator, induces variations of the elementary magnetic moment and of the exchange interactions. The variation of the magnetic moment is reflected in particular in the change of the saturation magnetization, but since this property is very sensitive to slight anisotropic stresses, the corresponding experiments must be conducted in a truly hydrostatic environment in order to obtain significant results. The variation of exchange interactions is reflected in the pressure shift of the Curie temperature which is, to the first order, insensitive to anisotropic stresses. Hence it is possible to determine experimentally the shifts of Curie temperatures induced by the very high pressures which can be produced inside a solid compressive medium giving only a quasihydrostatic environment. Such pressures, of the order of 100 kbar or more, produce relatively important volume changes; for example, application of a pressure of 100 kbar to a metal produces a decrease in volume equivalent to that obtained by a cooling of about 1500 °K, and this without any secondary disturbing effect.

On the other hand, some progress has been made in the last few years in the theory of band ferromagnetism for 3*d* transition metals, so it is now possible to calculate theoretically the effect of pressure on Curie temperatures in two particular cases: strong itinerant-electron ferromagnets with a few carriers, such as nickel, or very weak itinerant-electron ferromagnets, such as Invar-type alloys.

The pressure effect on the magnetic properties, mainly saturation magnetization and Curie temperature, has been investigated for a long time. Generally the effects are very small and the first results were erratic. The first real attempt, truly aimed at the determination of the shift of a transition temperature, was made by Adams and Green in 1931.[1] These authors studied several ferromagnets, iron and nickel in particular, by monitoring the thermal variations of the initial magnetic permeability. From their results they concluded that the Curie temperatures investigated remained unaffected by pressure. Other experimentalists obtained the same result, although they used different methods, namely, measurement of the electrical resistivity or of the magnetization.[2,3] The first coherent results were obtained in 1954 by Patrick,[4] who studied up to 8 kbar iron, nickel, and cobalt, among other ferromagnets. Since this time many experiments have been made to determine the pressure effect on Curie temperatures.[5,6] Most of them were restricted to pressures below 10 kbar and were generally devoted to ferrites or rare-earth metals. From the results it has been possible to calculate how the exchange interactions vary with volume. Recent work performed at higher pressure yielded the Curie-temperature shifts of rare-earth metals and their alloys up to about 80 kbar.[7] In this case the low values of the Curie temperatures allow one to cool the pressure vessel from the outside. Improved high-pressure techniques, mainly the use of an apparatus with a larger cell, which makes possible the heating from the inside, allowed us to study metals which have high Curie temperatures. Partial results of our work on 3*d* transition metals and alloys up to a maximum pressure of 90 kbar have previously been reported in brief notes.[8–10] In the present article we will describe and discuss the details of this work. The study of alloys in connection with that of pure metals gives additional information necessary for testing the range of validity of theories proposed up to this time to explain the Curie-temperature shifts for pure metals. Furthermore, the considerable extension of the pressure range allows a better estimate of the shifts and also displays some new features which proved to be essential in the understanding of the alloys themselves (Invar, for example).

II. EXPERIMENTAL

The pure metals were of spectroscopic grade and were supplied by Johnson-Matthey Ets. Two of the nickel alloys were of commerical grade (30- and 36-wt% Ni) and their impurity content was less than 0.8 wt%. All the others were made by induction melting in vacuum, the impurity content being less than 0.2 wt%.

The Curie temperatures were measured by a method formerly used at moderate pressures.[4] The sample which is submitted to the pressure P and the temperature T has a toroidal shape and forms the core of a microtransformer (Fig. 1). An ac current of constant amplitude flows in the primary coil. The secondary voltage is directly proportional to the initial magnetic permeability. A frequency of 1 kHz is used. The temperature is measured with a chromel-alumel thermocouple, the hot junction of which is in contact with the sample. The permeability μ is recorded as a function of temperature at various pressures. It increases sharply and goes through a maximum, the Hopkinson's maximum, just before the Curie point and then drops off. We define the Curie point as being the inflexion point of the curves $\mu = f(T)$ or as the middle point between extremum values when the curves are slightly modified by the effect of pressure. This method, with no magnetic field bias applied, does not allow a conven-

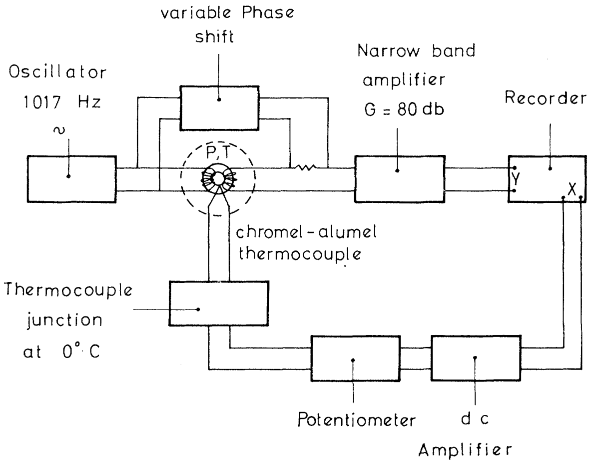

FIG. 1. Schematic drawing of the equipment used in Curie-point determination.

tional determination of the Curie temperature, but it is able to give with accuracy the variations of the Curie point. In Fig. 2, the permeability curves obtained for pure nickel are shown. The discontinuities are always very sharp and the Curie points can be easily defined. The small tails which can be seen on the high temperature side, especially at moderate pressures, come from the anisotropic stresses due to the use of a solid pressure-transmitting medium. These stresses also explain that the height of the Hopkinson's maximum varies with pressure. No account is taken of this effect since it is possible to drastically increase the signals by heating the sample briefly to around 700 °C under pressure.

Pressure is produced in an apparatus of the belt type. The details of the pressure cell are indicated in Fig. 3. The pistons are protected from excessive heating by small disks made of steel and alumina. The sample ($\varphi_{\text{o.d.}} = 3.3$ mm, $\varphi_{\text{i.d.}} = 1.3$ mm) with the two windings is placed in the center of the cell. One single coil contains the two windings. This coil is made of a "thermocoax" cable: Inside a stainless-steel tube there are two thermocouple wires insulated with magnesia. The external diameter is 0.34 mm. This type of cable is very convenient under high pressure because it can sustain a great deal of deformation without breaking or making a short circuit. Talc is used as the pressure-transmitting medium. The temperature is monitored with a chromel-alumel thermocouple also made from a thermocoax cable, but with a larger diameter (0.5 mm). All the wires come out from the pressure cell by passing through the gaskets. Heating is provided by means of a tubular graphite resistor. A high-intensity alternating current, controlled by a saturable inductance, is used. At temperatures above 1000 °K talc, which would decompose and damage the thermocouple, is replaced by boron nitride and use is then made of two distinct coils.

The pressure is measured in the usual way: At room temperature the electrical resistances of wires of bismuth, thallium, and barium are monitored as a function of the load in special cells where the compressibility has been adjusted to be

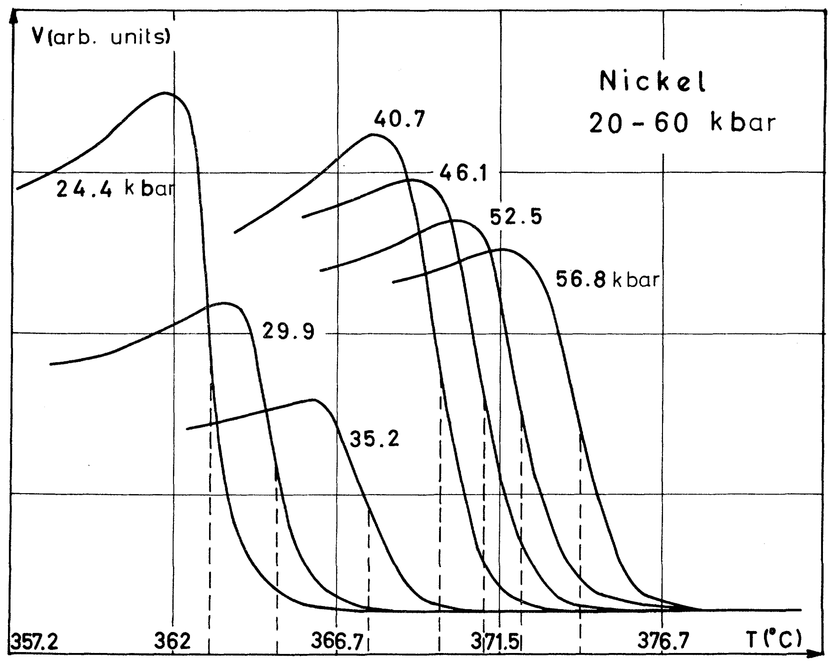

FIG. 2. Relative secondary voltage as a function of temperature for pure nickel at different pressures. The amplitudes of the curves recorded at 40.7, 46.1, 52.5, 56.8 kbar have been multiplied by ten.

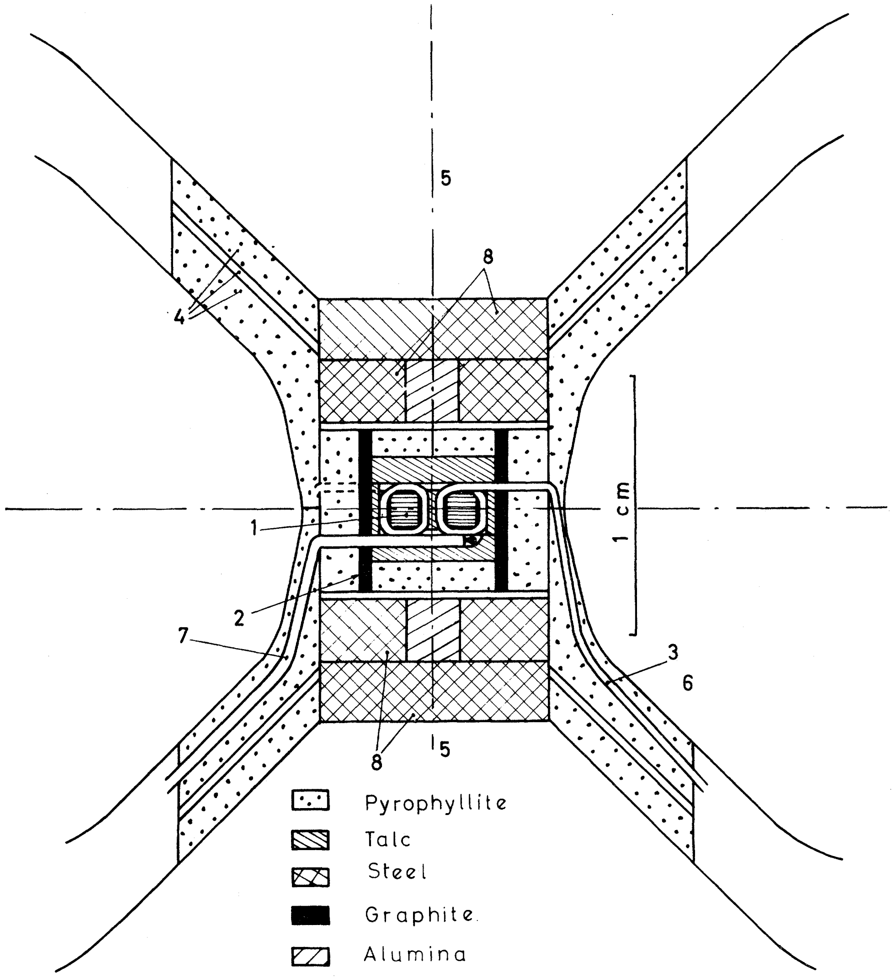

FIG. 3. Measurement cell for determining the shift of Curie temperature with pressure: 1, toroidal sample; 2, carbon heater; 3, measurement windings; 4, composite gasket; 5, carboloy pistons; 6, carboloy core; 7, chromel-alumel thermocouple; 8, thermal protective disks.

close to that of the cells used for the measurements. The following pressures are used for the polymorphic transitions occurring in these metals: Bi_{I-II} 25.4 kbar, Tl_{I-II} 36.7 kbar, Ba_{I-II} 55 kbar, Bi_{III-V} 77 kbar. Without taking into account the variations of the pressure scale, we estimate that the pressure accuracy is about 3% above 20 kbar and 1% below 20 kbar.

For the temperature measurements, the chromel-alumel thermocouple has been chosen because of the very weak pressure effect on its emf. Since most experimentalists used this kind of thermocouple and did not take account of this effect, we do not include the corresponding correction in our results, except particular notice and so comparison between data is simplified. Neglecting the above-mentioned correction, the estimated accuracy of the Curie-temperature shifts is better than 0.5 °C above 20 kbar.

The experimental technique just described presents some advantages over techniques where electrical resistance[11] is measured or where differential thermal analysis[12] or differential thermal-conductivity analysis[13] can be used. Indeed in our experiments the thermal gradients across the sample appear to be negligible since they cannot be detected even at 1400 °K. This is probably due to the sample geometry and to the fact that our measurements can be made with a heating or cooling rate as low as desired; this is impossible when thermal measurements are made because of the high thermal losses in the small high-pressure cells. In addition, insulators and metals, as well as powder compounds, can be studied.[14] Finally, the observed discontinuities are very sharp and allow a good determination of the transition points.

III. RESULTS

A. Pure 3*d* Metals

The Curie point of iron does not vary with pressure up to 17.5 kbar, where it meets the α-γ boundary (Fig. 4). The experimental data can be represented by the following expression:

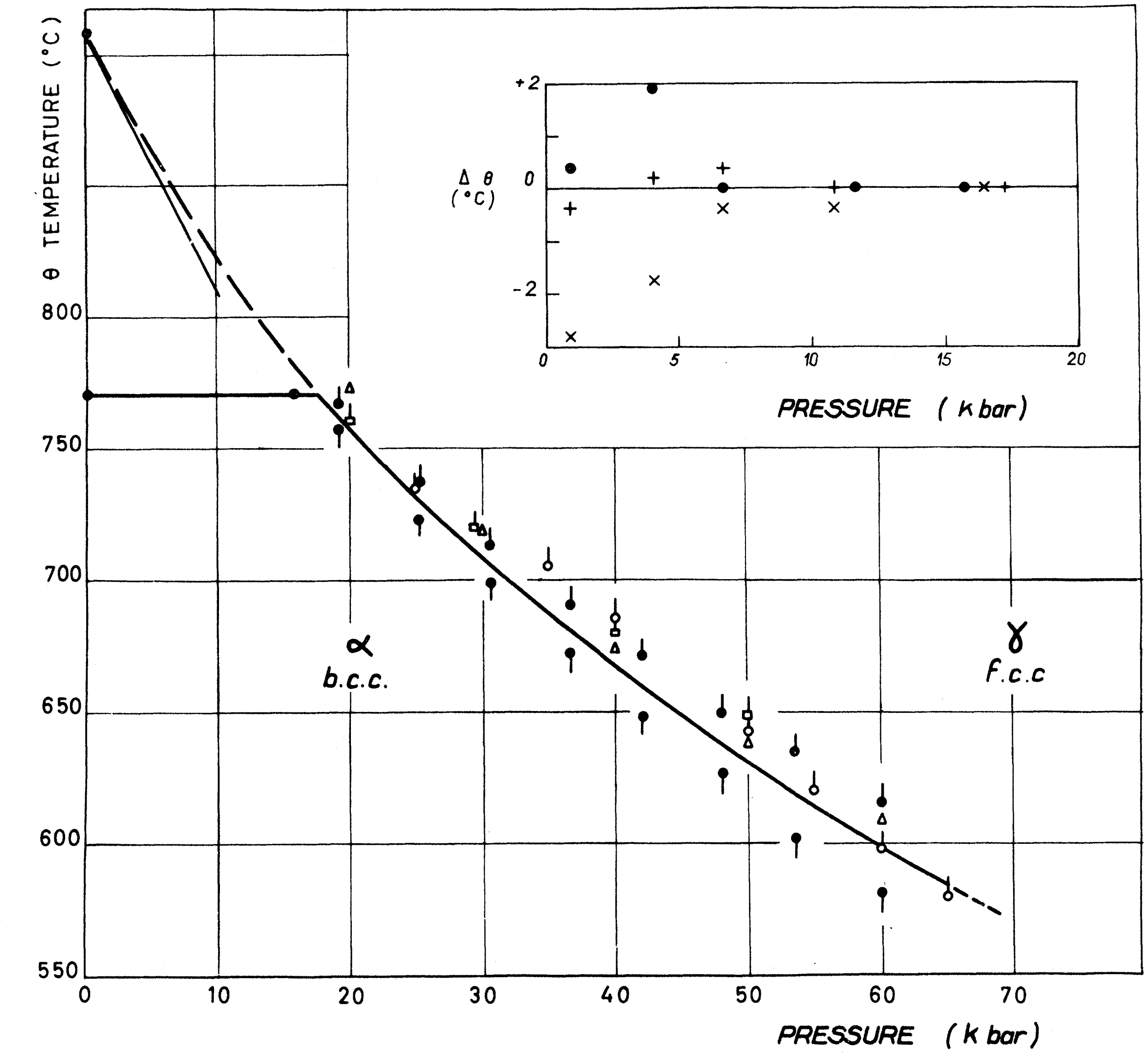

FIG. 4. Curie temperature and α-γ phase boundary of pure iron as a function of pressure. In this case the pressure scale is as follows: Bi_{I-II} 25.4 kbar, Ba_{I-II} 58.6 kbar. (In the insert are shown three different series of measurements for the shift of the Curie temperature. The temperature scale has been enlarged 10 times.) Magnetic determination of the α-γ boundary: $\overset{|}{\bullet}$, heating and $\underset{|}{\bullet}$, cooling; electrical resistance (heating) $\overset{|}{\circ}$ (Kaufman); DTA (heating) $\overset{|}{\square}$ (Kennedy); DTCA Δ (Claussen).

$$\frac{d\theta}{dP} = (0 \pm 0.03)\ ^{\circ}\mathrm{K/kbar}\ .$$

The α-γ boundary, which was obtained in the same way as the Curie point, is thought to be determined with a greater accuracy than in previously reported works because of the better experimental conditions mentioned above. The average curve of the transformation (center of the hysteresis region) has been joined to the known transformation point at ordinary pressure and has been fitted to the tangent[15] at atmospheric pressure calculated from the Clapeyron equation. The width of the hysteresis region increases with pressure. According to the observed transition, there is a marked difference in the permeability: At the Curie point the curves recorded at increasing or decreasing temperature cover each other exactly (for pure nickel or cobalt the situation is identical), whereas at the α-γ transformation a hysteresis region is always present.

For cobalt, no variation of the Curie temperature appears under the effect of pressure up to 60 kbar:

$$\frac{d\theta}{dP} = (0 \pm 0.05)\ ^{\circ}\mathrm{K/kbar}\ .$$

The Curie point of nickel has been determined up to 90 kbar (Fig. 5). It increases with pressure in a nonlinear way, especially above 60 kbar. It is the only known example of a pure metal behaving in such a manner. If the shift of the Curie temperature is plotted as a function of volume instead of pressure, the curve $\theta(V)$ is also concave toward the V axis.

At low pressures the experimental data can be expressed as

$$\frac{d\theta}{dP} = (0.36 \pm 0.02)\,^{\circ}\mathrm{K/kbar}\ ,$$

but at 80 kbar the slope is less than half this value being only $(0.17 \pm 0.02)\,^{\circ}\mathrm{K/kbar}$.

The values of $d\theta/dP$ for the pure $3d$ ferromagnetic metals measured by the different authors are given in Table I. At low pressure the present results agree well with the previous ones and for pure iron and cobalt the present data are even more accurate. This is due to the extended pressure range that has been explored. At pressures greater than 10 kbar there are no previous results.

B. Iron-Nickel Alloys

We studied the iron-nickel alloys having the same structure as pure nickel (fcc). It is well known that they exist only when the relative nickel concentration is greater than about 30 wt%. Their Curie temperature is strongly dependent on the nickel content and goes through a maximum at about 880 °K for 68-wt% Ni.

The observed pressure shifts are shown in Fig. 6. For most of the alloys the shifts are nonlinear, but exhibit some curvature. For Invar (36-wt% nickel) the variation of the Curie point follows a parabolic law. When the nickel content is low (30–40 wt%) the Curie point is decreased very markedly by pressure. This decrease becomes smaller and smaller as the nickel content is increased. When it is over 68 wt%, the Curie temperature increases with pressure, at least in the lower pressure range. For the alloy containing 75-wt% nickel a maximum is observed near 35 kbar, and in view of the concavity of the other curves, it is probable that such maxima do exist for the other alloys and perhaps even for pure nickel at higher pressure. In Fig. 7, the results are shown as a function of composition. One can see that the initial slope $d\theta/dP$ becomes zero for the alloy which has the greatest Curie temperature. In the Invar range (30–40-wt% Ni) the slope is closely proportional to the inverse of the Curie temperature itself.

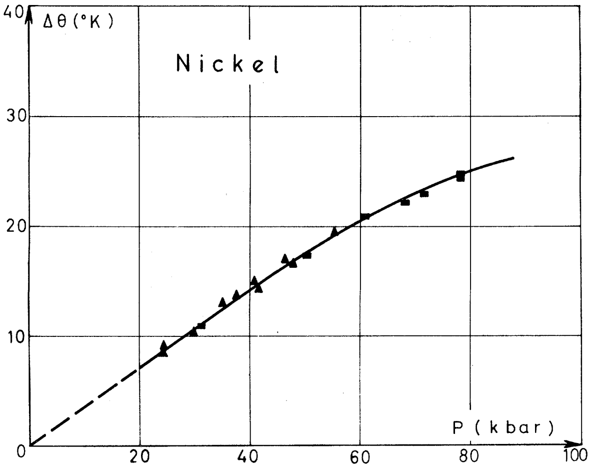

FIG. 5. Shift of the Curie temperature of nickel with pressure. (Two sets of determinations.)

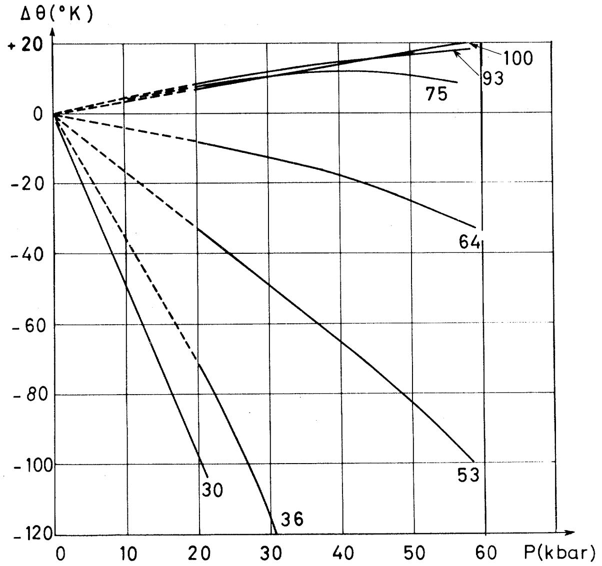

FIG. 6. Pressure shift of the Curie temperature of face-centered-cubic alloys of nickel with iron. (The number near each curve is the weight-percent content of nickel.)

C. Cobalt-Nickel Alloys

Alloys of nickel with cobalt exist over the whole composition range and are all face-centered cubic at the measurement temperatures. The Curie temperature decreases monotically from the value for pure cobalt (1398 °K) to the value for pure nickel (627 °K). Contrary to the previous case, we observed that the Curie point is always shifted upwards by pressure (Fig. 8). The greatest variation is obtained for an alloy which contains 45-wt% nickel, the initial slope being then 0.84 °K/kbar. In most cases, a concavity toward the pressure axis is observed and it may be supposed that maxima will exist at higher pressures as for iron-nickel alloys. In Fig. 9, the results are shown as

TABLE I. Curie temperature at atmospheric pressure and pressure shift $d\theta/dP$ for pure $3d$ transition metals. Comparison with previous data. (To obtain the real shift, the pressure effect on the thermocouple must be taken into account.)

Metal	Curie temperature (°K)	Pressure (kbar)	$\frac{d\theta}{dP}$ (°K/kbar) Present work	Patrick (Ref. 4)	Bloch (Ref. 5)	Okamoto *et al.* (Ref. 6)
Iron	1044	0	0 ± 0.03	0 ± 0.1	...	...
Cobalt	1398	0	0 ± 0.05	0 ± 1	...	...
		60	0 ± 0.05			
Nickel	627	0	0.36 ± 0.02	0.35	0.32	0.37
		80	0.17 ± 0.02			

a function of composition.

In Table II, the experimental data for the $3d$ transition metals and alloys are reported, no correction being made for the pressure effect on the emf of the chromel-alumel thermocouple. This correction is very small up to 800 °K but differs significantly from one author to the other above this temperature.[16–18] However, it never leads to a noticeable change of the experimental slopes. The correction to be added to $d\theta/dP$ is respectively + 0.05 °K/kbar for nickel, + 0.05 or − 0.08 °K/kbar for iron, and 0 or − 0.4 °K/kbar for cobalt according to the different published data. In the following discussion and in Fig. 10 where $d\theta/dP$ is plotted as a function of θ, the results have been corrected using the data of Hanneman and Strong.[16]

IV. DISCUSSION

A. Thermodynamics: Ehrenfest's Relation

Once the shift of the Curie temperature under the effect of pressure has been experimentally de-

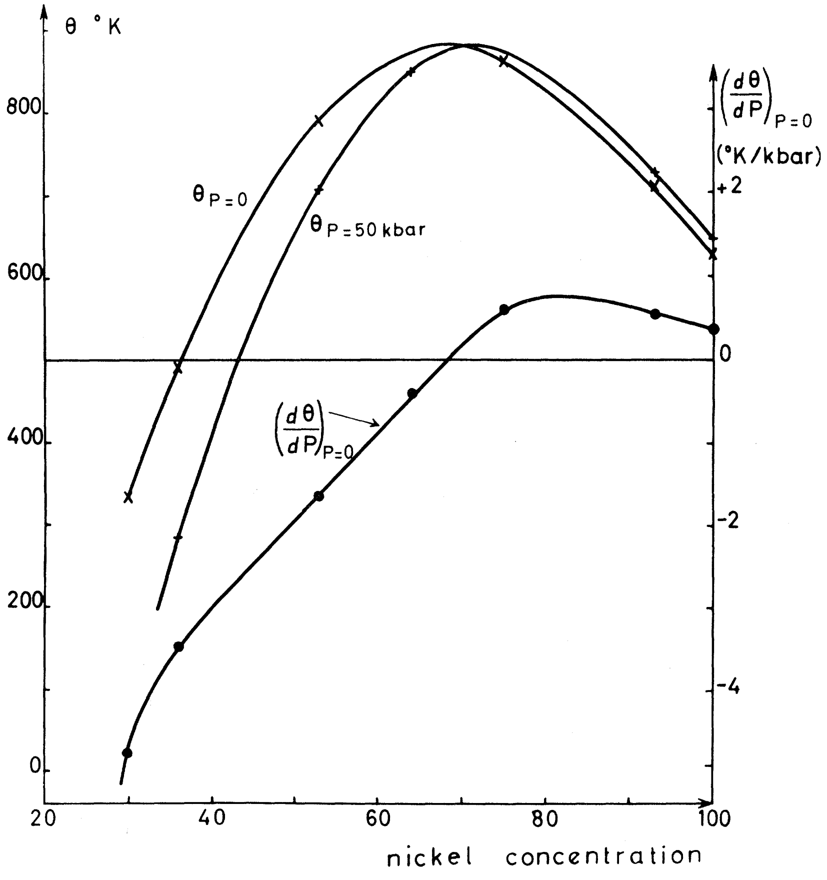

FIG. 7. Curie temperature θ and slope $d\theta/dP$ for iron-nickel alloys as a function of the nickel content (weight percent).

TABLE II. Curie temperature at atmospheric pressure and initial pressure shift $d\theta/dP$ for 3d transition-metal alloys.

Composition (wt%)	Curie temperature θ (°K)	$\frac{d\theta}{dP}$ (°K/kbar)	Composition (wt%)	Curie temperature θ (°K)	$\frac{d\theta}{dP}$ (°K/kbar)
Iron	1044	0	Cobalt	1398	0
30 Ni-70 Fe	334	−4.9	30 Ni-70 Co	1219	+0.55
36 Ni-64 Fe	491	−3.5	45 Ni-55 Co	1125	+0.84
53 Ni-47 Fe	788	−1.66	60 Ni-40 Co	1022	+0.76
64 Ni-36 Fe	873	−0.40	75 Ni-25 Co	903	+0.68
75 Ni-25 Fe	858	+0.60	93 Ni-07 Co	723	+0.66
93 Ni-07 Fe	708	+0.52	Nickel	627	+0.36

termined, it can be compared with variations of other quantities through the relations provided by thermodynamics. In general a Curie point is taken as being a second-order phase transformation ($\Delta V = 0$, $\Delta S = 0$) so that Ehrenfest's relations apply. At constant magnetic field it can be written

$$\frac{d\theta}{dP} = V\frac{\alpha_A - \alpha_B}{C_{pA} - C_{pB}} = \frac{k_A - k_B}{\alpha_A - \alpha_B}\,, \tag{1}$$

where A, B are indices representative of the two phases, α is the coefficient of thermal expansion, k is the isothermal compressibility, and C_p is the isobaric specific heat.

For nickel all the quantities appearing in Eq. (1) have been independently determined and the agreement between the values of $d\theta/dP$ calculated [0.2 (Ref. 19) and 0.4 (Ref. 20) °K/kbar] or measured [0.41 °K/kbar (present work)] is very good when the accuracy of the measurements is taken into account. For iron the shift of the Curie temperature is more difficult to establish from measurements of the thermal expansion coefficient and specific heat. However, a negative value of $d\theta/dP$ can be deduced from a recent determination of α,[21] and using specific-heat measurements by Dench and Aliis[22] a value of the order of −0.1 °K/kbar is obtained. This negative slope would agree with that deduced from our experimental results using the correction for the pressure effect on thermocouples proposed by Getting and Kennedy,[18] which seems to be valid in the pressure and temperature range of interest here.

For pure cobalt, the available data lead to a value of $d\theta/dP$ which disagrees strongly with the experimental one. A more careful study of the Curie point at ordinary pressure seems necessary.

In the case of alloys it is generally impossible to make the preceding comparisons because some of the experimental data required do not exist.

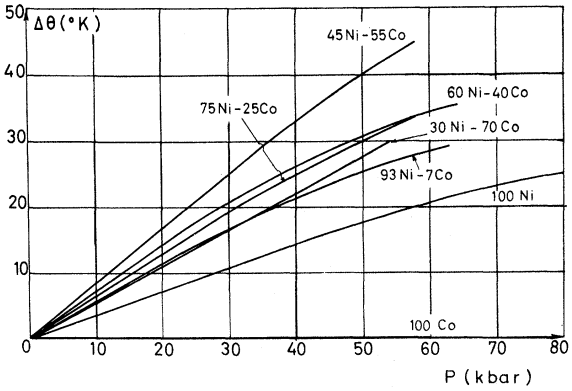

FIG. 8. Pressure shift of the Curie temperature of alloys of nickel with cobalt.

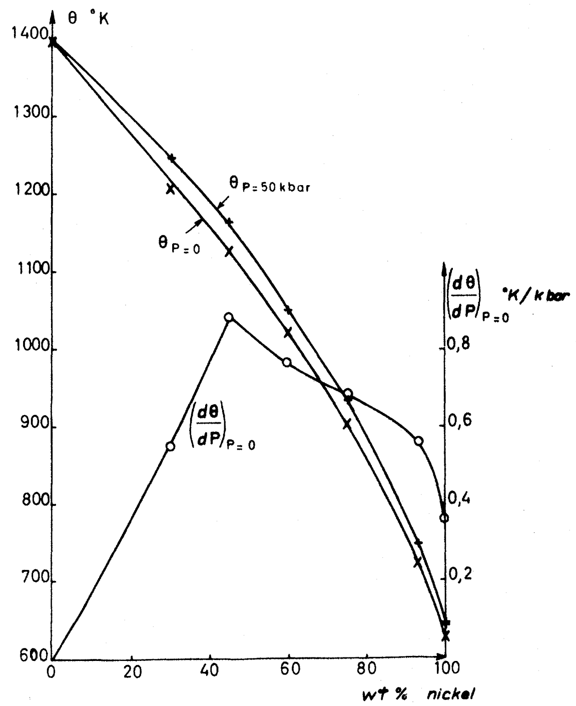

FIG. 9. Curie temperature θ and slope $d\theta/dP$ for cobalt-nickel alloys as a function of the nickel content (weight percent).

B. Calculation of Shifts of Curie Temperatures

1. *Nickel*

A direct calculation based on band-structure and itinerant-electron theory has been carried out by Lang and Ehrenreich for strong ferromagnets only in recent years.[23] For nickel the calculation is possible because the 3*d* band is nearly full, leaving only 0.6 hole per atom. The variation of the Curie temperature with pressure is deduced from the shift of the pole of the paramagnetic susceptibility with volume. An interaction Hamiltonian is used, its main feature being that the interaction between two *d* electrons is only noticeable when these lie in orbitals bounded to the same atom. This assumption arises from the very low overlap of orbitals from adjacent sites and from the screening effect of conduction electrons. The *d*-band structure of nickel in the paramagnetic state is taken from Hodges *et al.*[24] Moreover it is supposed that the width W of the *d* band only depends on interatomic distances and varies in such a way that $d\ln W/d\ln V = -\frac{5}{3}$. This assumption has been experimentally verified in the case of copper and it gives ground to the following hypothesis: The *d* band uniformly widens as the crystal is compressed.

In a first step two additional assumptions have been made to obtain a simpler model: (i) The conduction band is neglected. (ii) The intraorbital correlation force U is supposed to be infinite.

Under these assumptions one obtains

$$\frac{d\ln\theta}{d\ln V} = -\frac{5}{3} \quad \text{or} \quad \frac{d\theta}{dP} = \frac{5}{3}k\theta \tag{2}$$

(k = compressibility).

For pure nickel the result deduced from Eq. (2) is $d\theta/dP = +0.60$ °K/kbar, which agrees relatively well with the experimental value at low pressure: 0.41 °K/kbar. But when the pressure increases the agreement is no longer satisfactory; at 80 kbar, for example, the experimental result is then only +0.22 °K/kbar. This itinerant-electron theory is at the present stage unable to explain the curvature we observed on the curve $\theta(P)$; it even would predict a slight curvature in the opposite direction.

Does the introduction of the effects of the conduction band, of the interorbital interactions, and of the finite strength of the intraorbital interactions result in better agreement with experiment? The calculation has been made in this case,[23] but the result is then obviously dependent on the assumed strength of the interactions and on the *d* band structure. For an intra-atomic interaction U of 3.9 eV, the computed slope $d\theta/dP$ is now 0.33 °K/kbar (0.33 and not 0.38 as stated in Ref. 23 because the value of the compressibility of paramagnetic nickel is only 0.57×10^{-3} instead of 0.64×10^{-3} kbar as assumed).[25] This value is now lower than the experimental result at low pressure, but use of the more generally accepted value 5 eV for U would lead to a higher value for $d\theta/dP$ which will then be closer to the measured one.

2. *Iron and Cobalt*

For pure iron and cobalt, the preceding theory is no longer reliable, mainly because the carriers are more numerous. The calculated results from the simpler model would be, respectively, +0.96 and +1.2 °K/kbar, both of which greatly disagree with experiments. It has not yet been possible to carry out a calculation for these two metals.

3. *Nickel-Cobalt Alloys*

The result obtained from the simpler model is very useful because it is independent of the shape of the *d* band, so that it is easily applicable to different metals or alloys which are strong ferromagnets. In particular it can be compared to the experimental results on nickel-cobalt alloys which have been studied. In order to make the comparison easier, the slope $d\theta/dP$ is shown in Fig. 10 as a function of the Curie temperature rather than of composition. The experimental data for nickel-cobalt alloys now lie on two straight segments. In a wide range of composition, from 5- to 50-wt%-cobalt content, the shift of the Curie point of nickel-cobalt alloys is well described by the above simpler model. On the other hand, above 50-wt%-cobalt concentration a sudden decrease of the slope $d\theta/dP$ is noticed. This may be ascribed to the nonvalidity of the susceptibility calculation in this range. Indeed, it is only reliable as long as the following condition is fulfilled: $n^{1/3}a \ll 1$ (n is the carrier density and a the radius of the interaction potential). This product is already equal to 0.3 for pure nickel and it increases with cobalt or iron content.

For nickel-iron alloys the experimental results cannot be described by relation (2). It can just be noticed that the maximum value of $d\theta/dP$ is approximately equal to the theoretical one.

The question then arises whether better results would be obtained with the more realistic model, but assumptions about the shape of the *d* band must then be made.

In the case of nickel-copper alloys[23] two models were tested: A rigid-band model where the only effective change is a shift of the Fermi level in the *d* band and a minimum-polarity model where it is supposed that each atom keeps the configuration it would have in the pure metal. The first model leads to an increase of $d\theta/dP$ with copper content instead of the experimentally observed

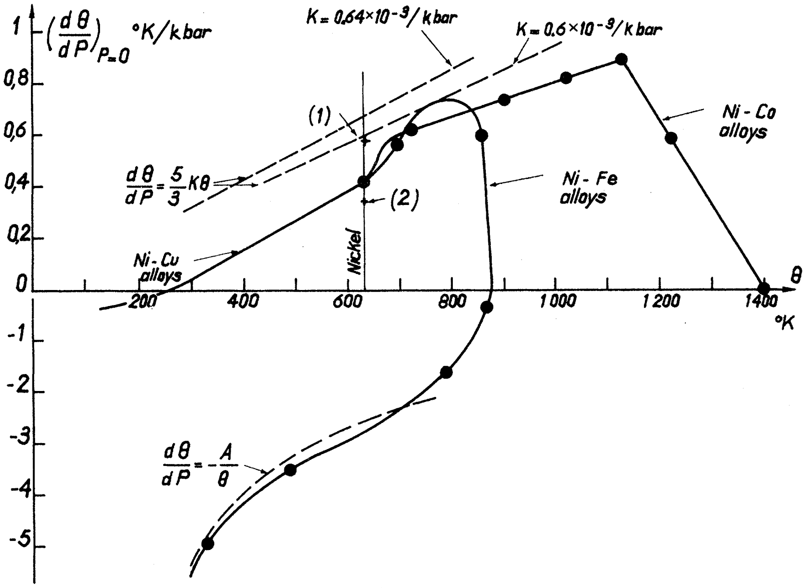

FIG. 10. Shift of the Curie temperature $d\theta/dP$ vs the Curie temperature itself. Theoretical, dash line with plus; experimental, solid line with dot. Notice the scale change for $d\theta/dP$ at the origin. K is the compressibility, 0.64×10^{-3} kbar^{-1} corresponds to iron-nickel alloys, 0.60×10^{-3} kbar^{-1} to cobalt-nickel alloys. The results for nickel-copper alloys are taken from Okamoto (Ref. 6). For pure nickel the simpler model gives the result labeled 1, the more realistic model the result labeled 2.

decrease, whereas the second one gives the right variation for $d\theta/dP$. These two opposite results are easy to explain, however, in the case of these alloys. For nickel-iron or nickel-cobalt alloys the corresponding calculations have not yet been performed, but it can be predicted that the two models will give essentially an increase of $d\theta/dP$ with iron or nickel content.

4. *Iron-Nickel Alloys: Invar*

The preceding theory is no longer valid for Invar-type alloys where the interactions are not strong but on the contrary are very weak. The shift of the Curie temperature has been computed by Wohlfarth in the framework of the Stoner's theory and it is given by the following equation[26]:

$$\frac{d\theta}{dP}=-\frac{A}{\theta}\ , \tag{3}$$

with

$$A=2kCNN(E_F)\mu_B^2T_F^2\ ,$$

where k is the compressibility, N is the number of atoms per unit volume, μ_B is the Bohr magneton, $N(E_F)$ is the state density at the Fermi level, T_F is the degeneracy temperature which depends on the shape of the d band and is much greater than the Curie temperature, and C is a constant which introduces magnetoelastic phenomena in the expression of the free energy.

The study up to 10 kbar of the pressure shift[27] of the Curie temperature of Invar-type alloys showed that relation (3) was very well satisfied in a large range of Curie temperatures and, in addition, it showed also that the quantity A remained a constant when the element alloyed with iron was changed (Pt, Pd, Ni), its value being about 1700 °K^2/kbar. Under these conditions we estimated that A would not vary with volume or pressure, although the d band is then modified in a slightly different way. We then easily derived the following expression:

$$\theta^2=\theta_0^2(1-P/P_0)\ \text{with}\ P_0=\theta_0^2/2A\ , \tag{4}$$

where θ_0 is the Curie temperature at zero pressure, and P_0 is the pressure above which ferromagnetism would no longer exist.

The parabolic shift of the Curie temperature which is predicted by relation (4) has actually been observed by us for the alloy named Invar ($Ni_{0.36}Fe_{0.64}$) up to 60 kbar (the maximum pressure then available in our measurements) and for a total change of the Curie temperature of the order of 250 °K (Fig. 11). The extrapolated value

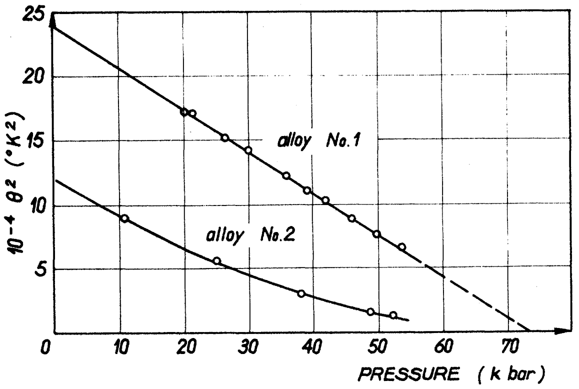

FIG. 11. Square of the Curie temperature as a function of pressure for two Invar alloys: alloy No. 1, Ni_{36}-Fe_{64}; alloy No. 2, $Ni_{0.30}$-$Fe_{0.70}$.

of P_0 is 72 kbar, which is very close to the predicted value of 71 kbar. On the other hand, for an alloy containing only 30-wt% nickel such a parabolic decrease has not been observed, but it must be emphasized that the composition is then close to the critical one where all properties of iron-nickel alloys are drastically modified. Further experiments are under way to test the validity of relation (4) for a wide variety of Invar-type alloys.

It has also been observed that pressure decreases strongly the Curie temperature of $ZrZn_2$, which is an Invar-type alloy. It seems that the shift in this case can also be fitted by a parabolic law, [28] but in addition, as the Curie temperature is low, it has been possible to determine experimentally that the alloy is no longer ferromagnetic above P_0, which is in this case about 6 kbar—that would confirm our results. Furthermore it can be justified that the quantity A is roughly a constant[29] when pressure varies.

5. *Iron-Nickel Alloys Other than Invar*

The above theory which predicts a rapid decrease of the Curie temperature under the effect of pressure is no longer valid when the nickel concentration increases over 45% since the strengths of the interactions increase at the same time. To give an account of the properties of iron-nickel alloys a model has been proposed by Weiss[30] where it is supposed that iron in the γ state has two different electronic levels and that each atom entering an alloy keeps the configuration it would have in the pure metal. This model gives satisfactory results at ordinary pressure and also it can yield a contribution to $d\theta/dP$ which would represent the effects of the two states of γ-iron.

If this calculated value of $d\theta/dP$[31] is subtracted from the experimental result, we get a value which represents the shift $d\theta/dP$ for an alloy in which γ-iron would have only one electronic level. Extrapolating to pure ferromagnetic γ-iron (one γ state only) yields for $d\theta/dP$ the value +1.5 °K/kbar, which is approximately the value one can get from the simpler model if the Curie temperature is then assumed to be 1800 °K as estimated from different approaches. This model has been used to describe a lot of properties of the iron-nickel alloys or even of cobalt-iron alloys but it lacks a theoretical base.

V. CONCLUSION

The transformer method has been adapted to the high-pressure techniques of the 100-kbar range, so that the shift of the Curie temperature of any metal or insulator can be determined. The temperature range extends from 77 to 1400 °K, but it would be possible to reach lower temperatures. This range of pressure allowed us to obtain new features for the shift of the Curie temperature of 3*d* transition metals. At low pressures the present results agree well with previous ones or are sometimes even more accurate. At higher pressures the shifts of the Curie temperatures are generally no longer linear, but exhibit some curvature toward the pressure or volume axis and this could not be seen with the previous experiments because they have been made in a too limited range of pressure. In one alloy the presence of a maximum has been established and that leads one to think that such a maximum can exist at very high pressures for pure nickel.

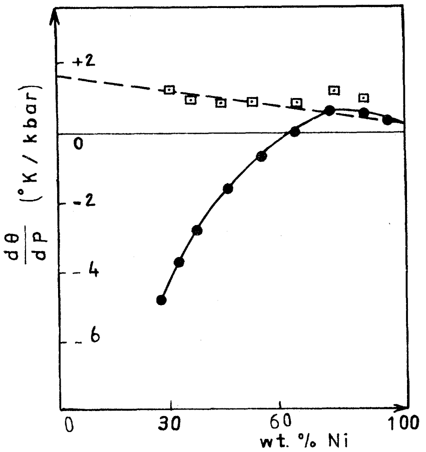

FIG. 12. Estimation of the shift $d\theta/dP$ in iron-nickel alloys in which γ-iron is supposed to have only one electronic level. Solid line with dot, experimental result; dash line with dotted square, effect of the two electronic states of γ-iron subtracted from the experimental results.

The itinerant-electron theory gives a reasonably good description of the experimental shift of the Curie temperature in some favorable cases, in particular, for very weak ferromagnets such as Invars. In this case, it appears that even the nonlinear dependence of the Curie point as a function of pressure can be explained and, in addition, it also shows that application of a sufficient pressure can rule out ferromagnetism in such alloys. For strong ferromagnets with few carriers only the shift in the vicinity of the ordinary pressure can be calculated with some confidence. In all cases the measured pressure shifts can be used as very sensitive tests regarding the various assumptions entering the theory in its present state (band structure, interactions, etc.). Moreover, although the nonlinear effects vs pressure or volume found in most of the alloys and in nickel at higher pressure lie presently outside the scope of the theory, they will undoubtedly stimulate further theoretical works in this field and help us to understand the behavior of ferromagnets at normal pressures.

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Spin Model with Antiferromagnetic and Ferromagnetic Interactions

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The one-dimensional Ising model with nearest-neighbor repulsion and infinitely long-range attraction acting only on even-numbered neighbors is solved exactly, using mean-field theory for the long-range part. Below a certain temperature one gets antiferromagnetic ordering. For temperatures giving antiferromagnetic ordering in zero magnetic field, there will be a phase transition from the antiferromagnetic to the more common ferromagnetic ordering for a finite magnetic field. The transition is of first or second order giving discontinuous magnetization or discontinuous susceptibility, respectively. It is shown by direct calculation that the second-order phase transition coincides with a divergence in the γ expansion for this model.

I. INTRODUCTION

Interest has recently arisen in two-parameter model Hamiltonians with competing short-range and very-long-range interactions; a rich variety of phase behavior has been found in these models.[1] In all these models the long-range interaction has been effectively of the Kac type,[2] and, in spin language, of the ferromagnetic type, encouraging all spins to align. This long-range part of the interaction can be treated rigorously by the Lebowitz–Penrose theorem.[2]

It was suggested to us by Lebowitz that it might be of interest to study models of a related type, in which the very-long-range interaction does not necessarily encourage ferromagnetic ordering.