nickel ferrite is significantly larger than that in the ferrite single crystals (Fig. 2), i.e., 315 oersteds. The difference may be attributed to the presence of internal strains and to demagnetization at the grain boundaries in the polycrystalline samples, the additional internal field of this origin being large enough to overcome the effects of the lower apparent magnetocrystalline anisotropy fields which must result from the random orientation of crystallites away from directions of easy magnetization.[16]

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[16] After this work was completed an article by R. Wangsness [Phys. Rev. 91, 1085 (1953)] appeared in which is given a formula equivalent to (6) except that it does not contain the distinction between the phenomenological anisotropy field and that which enters the resonance expression.

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The Change of Ferromagnetic Curie Points with Hydrostatic Pressure*

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The effect of pressure on the Curie temperature has been measured for 13 ferromagnetic materials, comprising 4 elements (Fe, Co, Ni, Gd), 7 metallic alloys, a ferrite, and a perovskite. Curie points ranged from 16°C (Gd) to 1120°C (Co), and pressures up to 9000 atmos. The results are in disagreement with two common forms of the interaction curve. The result obtained for Fe is not in agreement with the prediction of Kornetzki, based on volume magnetostriction measurements between 20°C and 100°C.

I. INTRODUCTION

Importance of Interatomic Distance

THE effect of pressure is considered to be that resulting from the change produced in interatomic distance, which is known to be an important parameter in the strength of magnetic interaction. Slater[1] first pointed out that ferromagnetism occurs only in those elements in which there is a large ratio of interatomic distance, D, to diameter of unfilled inner shell, d (usually a d shell, but in Gd it is the $4f$ shell). An accurate calculation of the magnetic interaction is still impossible at the present stage of the theory, but the several theoretical approaches all agree on certain qualitative features of the interaction curve (i.e., the curve showing the strength of the interaction as a function of interatomic distance).

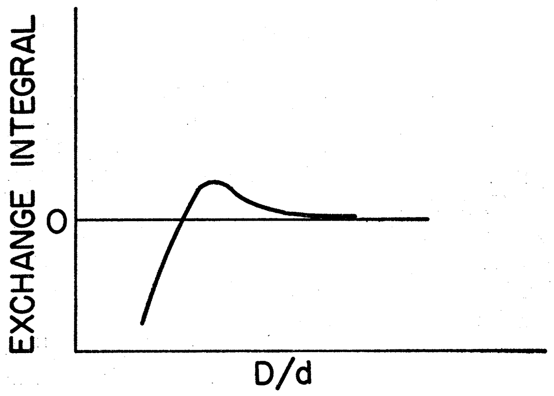

FIG. 1. Bethe interaction curve.

Sommerfeld and Bethe[2] discussed the type of wave function necessary to give a positive exchange integral in the Heisenberg theory, and they drew a curve (Fig. 1) to show qualitatively the features of this positive range. The band theory and Zener's theory both agree that ferromagnetism is not possible for very small or very large values of D, but the width of the ferromagnetic range is still an unsettled question. The salts of ferromagnetic elements, in which D is large, are paramagnetic rather than weakly ferromagnetic. On the other hand, Zener[3] has pointed out the importance of conduction electrons in coupling the d-shell spins. The salts may be paramagnetic because of the absence of conduction electrons.

The Forrer Correlation

Forrer[4] has made a correlation of magnetic interaction with interatomic distance, D, for Mn, Cr, Fe, Co, Ni and their compounds in which these elements retain their characteristic moments and in which coupling does not occur through intermediate atoms by the superexchange mechanism. He finds that as D increases the interaction changes, for each element, from antiferromagnetic to ferromagnetic and then to paramagnetic. The ferromagnetic range is roughly 10 percent

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[1] J. C. Slater, Phys. Rev. 36, 57 (1930).

[2] A. Sommerfeld and H. A. Bethe, *Handbuch der Physik* (J. Springer, Berlin, 1933), second edition, Vol. 24, No. 2, p. 596.

[3] C. Zener, Phys. Rev. 81, 440 (1951).

[4] R. Forrer, Ann. Physik 7, 605 (1952).

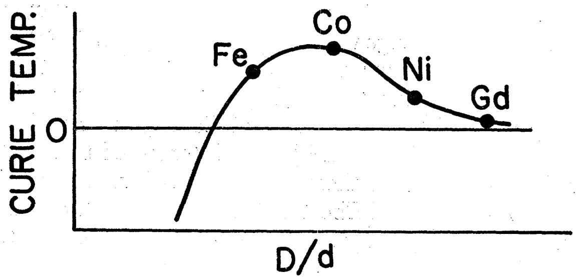

FIG. 2. Bozorth interaction curve.

of D—perhaps as little as 5 percent in Co. However, one must consider Zener's remarks about conduction electrons. The Forrer correlation overlooks the fact that the range of D in metals is rather limited. Dilution of ferromagnetic elements to increase the average distance does not work in metallic alloys because the conduction electrons of the added metal apparently fill the d band of the ferromagnetic element. The reduction of Curie point in such cases results from a reduction of average moment rather than from any distance effect. Perhaps the ferromagnetic range would be much greater than 10 percent if this range could be obtained in metals.

A narrow ferromagnetic range, as suggested by the Forrer correlation, has consequences for the present experiment. A pressure of 10 000 atmos, which is available in the laboratory for an experiment of this type, changes D by only about 0.2 percent, using an average value for the compressibility of metals. This means that it is impossible to measure any large portion of the interaction curve, but the change of Curie point with pressure does give the slope at a single point. If in Co the Curie temperature rises to 1400°K and falls to zero again within a range of 5 percent of D, the average rate of rise or fall must be over 10° per 1000 atmos. For Fe this figure is about 4°. This means that changes of this order of magnitude should be expected if the ferromagnetic range is as limited as Forrer suggests.

Interaction Curves

The Forrer correlation is an attempt to define the ferromagnetic range for single elements. The suggestion of Slater that D/d is the significant parameter for ferromagnetic interaction has led to attempts to draw a generalized interaction curve to include all ferromagnetic elements. The assumption is that D and d are the only important parameters in the strength of magnetic interaction; therefore a correlation is attempted, using a function of D and d as a "reduced" distance. Such attempts must prove futile if other important parameters exist (e.g., conductivity).

Figure 2 shows one such curve, drawn by Bozorth.[5] In this, Curie temperatures are plotted against D/d. However, the Curie temperature, on the assumption of a Weiss inner field, is proportional to μ^2N, in which μ is the atomic moment and N the Weiss field constant; and μ seems to be characteristic of the element, independent of D (the examples given by Forrer show this). Hence it would seem to be more logical to plot N as ordinate instead of the Curie temperature, in which case Ni, having the highest value of N, is at the top of the curve.

Néel[6] has plotted N/z against $D-d$, as shown in Fig. 3 (z is the number of nearest neighbors). He includes an antiferromagnetic range and has also extended the correlation to include interactions between different atoms in alloys. Fe, however, can be included only if it is assumed that next nearest neighbors are responsible for the ferromagnetism, the nearest neighbors being near the point where the curve crosses the axis, and therefore ineffective. He has found further evidence to support this curve; and has predicted an increase of Curie point with pressure in Fe of 0.79° per 1000 atmos and decreases in Co and Ni of 4.6° and 0.13°, respectively.

Reciprocal Effects

If a change of volume alters the magnetic interaction, there should be a reciprocal effect in which the change of intrinsic magnetization by a high field changes the volume of a ferromagnet. This effect has been measured as the volume magnetostriction, and more will be said of it later. Also, the loss of magnetization as the temperature is raised has an effect on the volume which shows up as an abnormal thermal expansion. This may be large enough, as in Invar, to compensate the normal thermal expansion over a certain temperature range. Both effects have been used to estimate the volume dependence of the interaction.

II. PREVIOUS RESULTS

There have been several unsuccessful or partly successful attempts to measure the change of Curie point with pressure. A short description of each of these will

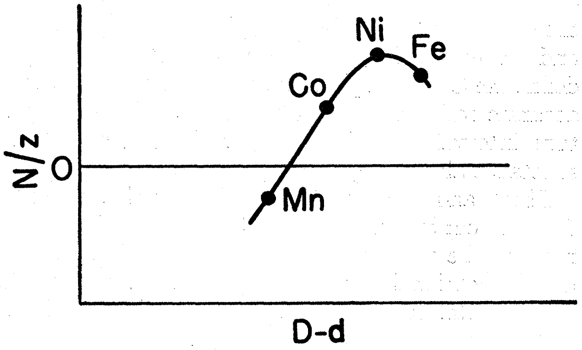

FIG. 3. Néel interaction curve.

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[5] R. M. Bozorth, Bell System Tech. J. 19, 1 (1940).

[6] L. Néel, *Le Magnétisme* (University of Strasbourg, Strasbourg, 1939), Vol. 2, p. 65.

be given. Following this, a summary will be given of estimates of the change to be expected, based on the indications obtained from volume magnetostriction data and from estimates of the anomalous thermal expansion.

Measurements Using High Pressure

In 1931, Adams and Green[7] used the method which has been adopted for the present experiment; they used the sample as the core of a transformer and, with a constant small alternating current supplied to the primary, they measured the output of the secondary as a function of temperature. The drop in output at the Curie temperature is very sharp, and although it does not define the Curie point in the conventional way, the method is very satisfactory for finding a *change* in Curie point. Unfortunately Adams and Green could not obtain a stable temperature in their pressure apparatus. CO_2 was used as a pressure fluid, and there were strong convection currents set up in it by the internal furnace. Their results indicate an uncertainty in temperature of about 5°, and this masked all changes.

Steinberger[8] did not attempt to measure the change of Curie temperature but observed a change from ferromagnetic to paramagnetic for a 30Ni 70Fe alloy (weight percent) under pressure applied at room temperature. The great change was undoubtedly due to a change of Curie point, but Steinberger described it in terms of a change in permeability.

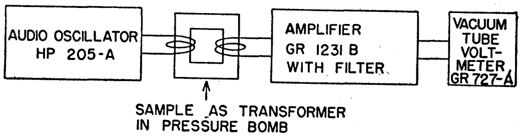

FIG. 4. Schematic diagram of experimental setup.

Michels *et al.*[9] have made measurements on two Monel alloys, using the change of slope of the resistance *vs* T curve as an indication of the Curie point. The ferromagnetic ordering lowers the resistance of a metal and results in a change of slope of the curve R *vs* T at the Curie point. This, however, is not sharp in practise, and an extrapolation procedure must be set up to define the Curie temperature. The method requires very accurate resistance measurements over large temperature intervals and is complicated by the fact that resistance also changes with pressure.

Ebert and Kussman[10] used large fields to obtain I *vs* T curves, using special nonmagnetic pressure bombs. The purpose was to define the Curie point in the conventional way under pressure; but the great experimental difficulties made accuracy impossible, and small changes could not be detected. In the alloy in which a large change was to be expected (30Ni 70Fe) the I *vs* T curve drops so slowly that the conventional method of defining the Curie point is not very useful. They decided that no change of Curie point had been observed, but Kornetzki[11] later reinterpreted their data and concluded that there had been a change of Curie point. A criticism of Ebert and Kussman's methods and conclusions has been given by Michels and de Groot.[12]

Predictions Based on the Reciprocal Effects

The predicted changes of Curie point with pressure are based on measurements of the thermal expansion anomaly or on measurements of volume magnetostriction. The latter cannot be carried out at high temperatures; thus they actually indicate the volume dependence of the magnetic interaction at the temperature at which they are carried out. This will be discussed under the results on Fe and Fe-Si alloys.

Slater[13] has used the Clapeyron equation as if the transformation from magnetic to nonmagnetic state were first order. The equation may be written $d\theta/dp = \Delta V/\Delta S$, in which θ is the Curie temperature. The volume change is estimated from the thermal-expansion anomaly, and the disordering entropy may be calculated, assuming dipoles with two orientations. Only order of magnitude is hoped for. For Ni, Slater has estimated an increase of Curie point with pressure of 0.05° per 1000 atmos.

If the transition is treated as second order, the corresponding Ehrenfest relation is $d\theta/dp = 3TV\Delta\alpha/\Delta C_p$ in which α is the linear coefficient of expansion and C_p the specific heat. These quantities do not show sharp discontinuities at the Curie point but an extrapolation method must be used. For Ni, Michels and de Groot[12] used average values of several determinations of $\Delta\alpha$ and ΔC_p and estimated the increase of Curie point with pressure to be 0.35° per 1000 atmos, which is in agreement with the result obtained in the present experiment. Ni was the only element for which sufficiently accurate experimental data were available.

In order to relate volume magnetostriction and change of Curie point with pressure, Kornetzki[14] has used the thermodynamic relation $dV/dH)_p = -dM/dp)_H$, where M is the total moment, and the assumption that the magnetization per gram, σ, is given by a relation of the form $\sigma = f(T/\theta)$. The relation derived from these is

$$\frac{1}{\theta}\frac{\partial\theta}{\partial p} = \frac{1}{T}\frac{\partial\omega}{\partial H}\bigg/\left(\rho\frac{\partial\sigma}{\partial T} - \frac{3\alpha}{K}\frac{\partial\omega}{\partial H}\right),$$

in which ω is the fractional change of volume, ρ the density, α the linear thermal expansion coefficient, and

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[7] L. H. Adams and J. W. Green, Phil. Mag. **12**, 361 (1931).

[8] R. L. Steinberger, Physics **4**, 153 (1933).

[9] A. Michels *et al.*, Physica **4**, 1007 (1937); A. Michels and J. Strijland, Physica **8**, 53 (1941).

[10] F. Ebert and A. Kussman, Physik. Z. **39**, 598 (1938).

[11] M. Kornetzki, Physik. Z. **44**, 296 (1943).

[12] A. Michels and S. R. de Groot, Physica **16**, 249 (1950).

[13] J. C. Slater, Phys. Rev. **58**, 54 (1940).

[14] M. Kornetzki, Z. Physik **98**, 289 (1935).

K the compressibility. For Fe, Kornetzki made measurements of volume magnetostriction between 20°C and 100°C and predicted a decrease of Curie point with pressure of 5 to 10 deg per 1000 atmos.

III. EXPERIMENTAL PROCEDURE

Transformer Method

The experimental method used is similar to that of Adams and Green,[7] using the magnetic material as the core of a transformer, as demonstrated in Fig. 4, which shows the necessary equipment except for the pressure and furnace systems. The primary and secondary coils are wound on opposite arms of the picture frame sample so as to have very little direct coupling. The linkage is essentially through the sample only, and this fails at the Curie temperature.

A constant 1000-cy current is supplied to the primary, and the signal from the secondary is amplified, then measured as a function of temperature. The primary current was of the order of 0.1 amp, giving a magnetizing field of the order of 1 oersted; and the secondary voltage was amplified to about 10 v, then read on the vacuum-tube voltmeter.

The character of the output curve varies greatly from sample to sample but usually has the general features of Fig. 5. There is an inflection point between A and B and a very nearly linear portion in most cases from 90 percent of maximum output to 10 percent. If the maximum output remains the same under pressure, curves taken at different pressures are simply translated along the temperature axis by the amount of the change of Curie point, and this change is well defined even though the initial permeability curves are not used to define the Curie point itself. If the maximum output should change, a scale adjustment would have to be made before comparing the curves, and the interpretation would not be so simple. Fortunately no change over 10 percent in the maximum output under pressure ever occurred except in the two cases where it was difficult to get the sample in the usual form and Fe was used to complete the magnetic circuit. The initial permeability of Fe at room temperature is depressed by pressure, as was shown by Steinberger;[8] but near the Curie point the initial permeability seems to be unaffected by pressure.

The temperature range over which the drop from 90 percent of maximum output to 10 percent occurs is small in the elements (1.5° for Ni, as can be seen in Fig. 11); it is small in alloys if the Curie point does not depend much on the composition (as in 68 Permalloy); and it is small if the alloy is very homogeneous (as in Alumel, a fully annealed thermocouple wire). On the other hand Compensator alloy (70Fe 30Ni) is an example of a sample in which the drop occurs over a wide temperature range; nevertheless, the change under pressure is a simple translation along the temperature axis.

Measurements were made with different primary currents to verify that changes found were independent of the field. To detect irreversible effects, measurements were made with falling and with rising temperatures and after increases and decreases of pressure. No irreversible changes were found. Measurements were made at several pressures; within experimental error any changes were linear with pressure.

Pressure Equipment

In the application of pressure two separate sets of pressure equipment were used. One is designed to use a liquid as the pressure fluid, and the other is designed to use a gas; these will be referred to as the liquid system and the gas system.

A liquid system has been described by Bridgman.[15] It is used for temperatures up to 400°C, and the fact that an external furnace is used to heat the entire pressure bomb means that there is good temperature stability and a large gradient-free experimental region.

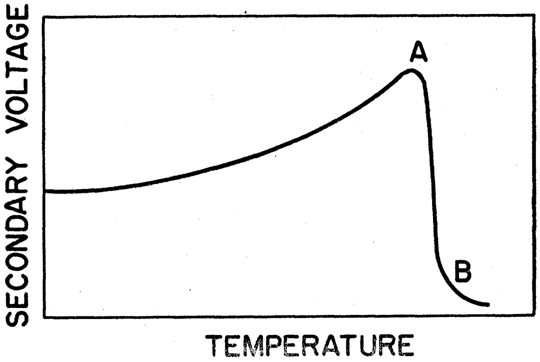

FIG. 5. General form of temperature dependence of voltage in secondary winding.

The gas system is used for higher temperatures (up to 1120°C). No liquid is known which will not decompose or react with other parts of the system at high temperatures; therefore an inert gas must be used, and argon has been found to be satisfactory. Also the hardened steel of the bombs softens with consequent rupture if it is heated for long periods at high temperatures. Therefore an internal furnace, insulated from the bomb, must be used. A gas system has been described by Yoder.[16]

Furnace Design

For the liquid system the whole bomb is heated externally. With an internal thermocouple it was found to be quite satisfactory to make measurements while allowing the temperature to drift at a rate of several degrees per hour. For Gd the bomb was cooled with dry ice, and measurements were made while it warmed up; this process took several hours.

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[15] P. W. Bridgman, *The Physics of High Pressure* (G. Bel and Sons, London, 1949).

[16] H. Yoder, Trans. Am. Geophys. Union **31**, 827 (1950).

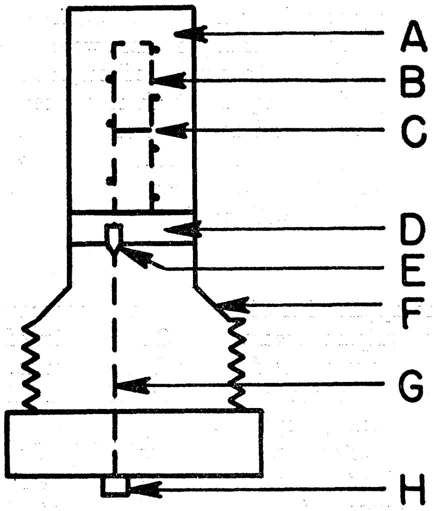

FIG. 6. Plug with furnace and insulation for gas system.

A. Lavite cylinder 3 in. high.
B. Furnace $2\frac{1}{2}$ in. high within lavite insulation.
C. Sample.
D. Lavite plate, insulating furnace from plug.
E. Electrically insulated cone at which a wire enters the high-pressure region.
F. Shoulder against which high pressure seal is made.
G. One of seven insulated wires entering bomb.
H. External electrical connection.

The furnace design for the gas system is much more critical. Three things must be kept in mind:

(1) Insulating material should be of the nonporous type, so as not to be penetrated by the argon under pressure. Lavite was found to be very good. The heat loss is more than doubled if ordinary firebrick is used.

(2) Convection currents in the argon must be cut down to avoid high heat loss and to achieve stable temperatures. For this purpose, Yoder[16] used a horizontal bomb. With a vertical bomb, the closed top furnace shown in Fig. 6 was found to use only half the power of one which ran the whole length of the lavite cylinder *A*; and the temperature stability was greatly increased.

(3) All space should be filled. This makes it easier to reach high pressures and also cuts down the convection currents. Lavite was used not only between furnace and bomb (*A* and *D* in Fig. 6) but also within the fused quartz cylinder (*B* and *D* in Fig. 7) to fill space on both sides of the sample.

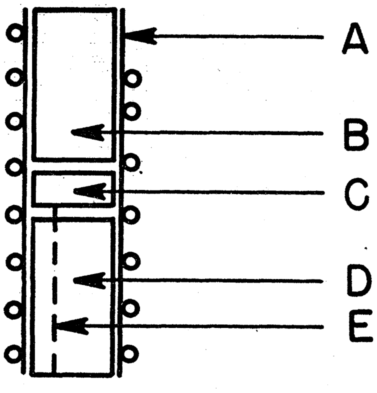

FIG. 7. Furnace with inner parts.

A. Fused quartz tube wound with 0.015 in. Pt wire.
B. Lavite cylinder above sample.
C. Ni ring surrounding sample.
D. Lavite cylinder below sample.
E. Electrically insulated wire from sample to cone.

The heat capacity of the furnace is small and the heat loss is high under pressure so that it is difficult to hold the temperature constant. Two variacs were used to control the input voltage; the second, in conjunction with a step-down transformer, permitted fine adjustment (7.5-v full scale) and the temperature could be controlled by voltage adjustment so that the rate of drift was about 1° in 3 min; this was good enough to permit fairly accurate readings of temperature and secondary output.

Sample Design

In the liquid system the size of sample is limited only by the internal dimensions of the bomb itself as this region is a uniform temperature. In the gas system, however, the bomb is cool (about 100°C) so that only a small region at the center of the furnace is gradient-free, and the sample must be quite small. It consisted of two rings of the shape shown in Fig. 8, maximum diameter about $\frac{1}{2}$ inch, held together by screws, and with the thermocouple wires between them. Total thickness is about 1/20 in. Mica rings of the same shape above and below provided insulation for the two windings, which were about 5 turns each of Chromel wire. This wire holds its shape well after being bent, and no cement was used. A nickel ring $\frac{1}{4}$ in. high (*C* of Fig. 7) which just fit into the quartz tube was used to surround the sample in order to smooth out the temperature gradients. This was separated from the sample by mica. When this assembly was placed at the hot spot of the furnace (*C* of Fig. 6), the sample was free of gradient, as could be verified by the sharp drop of secondary output at the Curie point. When the double-ring sample was placed in a temperature gradient, the drop occurred in two sections with a plateau at the half-way point. With no gradient in the sample, the temperature reading could be considered to be that of the sample, as the thermocouple wires then came out from

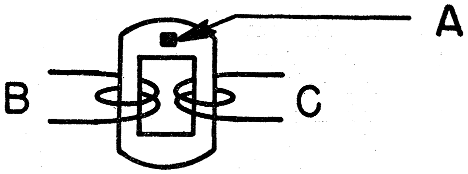

FIG. 8. Sample with windings.

A. Thermocouple junction between two rings.
B and *C*. Primary and secondary windings.

between the rings for about $\frac{1}{4}$ in. in a gradient-free region.

Temperature Measurement

For the liquid system it is convenient to have a thermocouple within the bomb, so that accurate measurements may be made while the temperature is drifting slowly. For the gas system an internal thermocouple is essential because of the large temperature gradients.

Birch[17] has investigated the effect of pressure on thermal emf, and the Chromel-Alumel couple was found to be independent of pressure within 10 microvolts as far as the calibration was carried (580°C and 4000 atmos). The entire path, including wire in the plug and the insulated cone (G and E in Fig. 6), must be of thermocouple wire. This is especially important in the gas system, as strong temperature gradients exist in just these places. It was found possible to obtain heavy Chromel and Alumel wire stock from which the cones were machined. However, there is still the problem that the complete circuit is made up of three different wires (the internal thermocouple, the cone, and the wire in the plug) and a perfect match of thermoelectric powers of these wires is impossible, so that a redistribution of gradients may look like a change of temperature. Such a redistribution does not occur in the liquid system when pressure is applied, but in the gas system the furnace power requirement doubles under pressure, and a redistribution of gradients is certainly to be expected. It was found that nearly all of the change in power requirement occurred between 1 and 400 atmos, and corresponding to this was an apparent Curie-point change of 2 or 3 deg. Hence measurements below 1000 atmos were not used. Measurements on Ni were made in both systems, and the results checked completely if data above 1000 atmos were used.

It should be emphasized that the precautionary measures are all for the purpose of measuring temperature *changes* under pressure. The Curie temperature itself does not enter into the experimental results and need not be known very accurately.

It will be noticed that measurements have been made using the thermocouple beyond its calibrated range; both temperature and pressure exceed the limits of Birch's calibration. The assumption is made that the thermoelectric power continues to be independent of pressure, but it would be desirable to have an extension of the calibration.

Pressure Measurements

Pressure measurements are made by finding the change in resistance of a Manganin wire gauge; this is the standard method and has been well calibrated.[18] The uncertainty (of about 0.1 percent) is insignificant in this experiment.

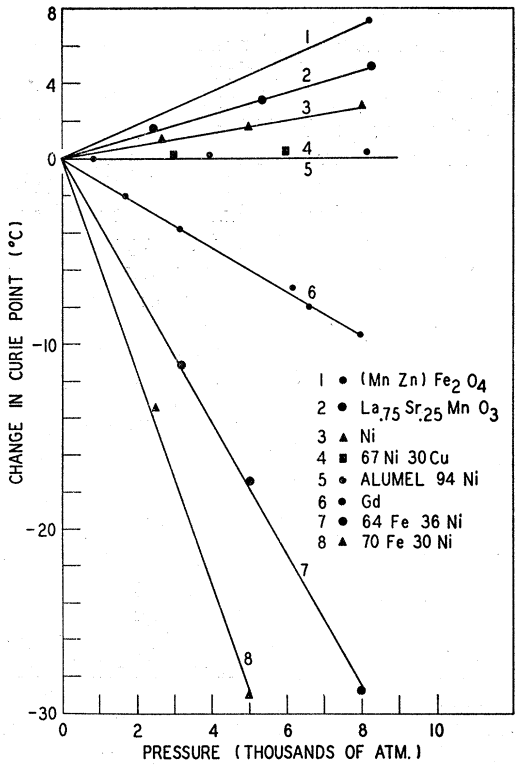

FIG. 9. Change of Curie point *vs* pressure for 8 samples measured in the liquid system.

IV. RESULTS

The results are given in Figs. 9 and 10 and in Table I. Figure 9 shows the change in Curie point *vs* pressure for the 8 samples for which the liquid system was used. Consistent results are obtained in each case although the change is so small for Monel and Alumel that it is about the same order of magnitude as the uncertainty

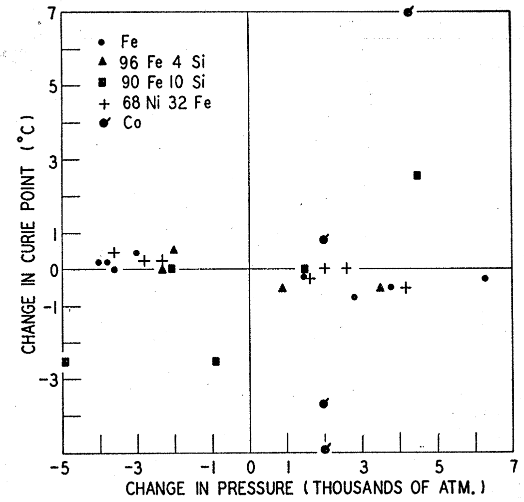

FIG. 10. Change of Curie point *vs* change of pressure for 5 samples measured in the gas system.

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[17] F. Birch, Rev. Sci. Instr. **10**, 137 (1939).

[18] David Lazarus, Phys. Rev. **76**, 545 (1949).

in Birch's pressure calibration of the thermocouple. Figure 10 shows the results for the 5 samples for which the gas system was used but plotted in a different way. As explained above, the readings for 1 atmos could not be used. Also the reproducibility was not as good as in the liquid system because of slow changes in the rate of heat loss or because of corrosion of the thermocouple wires. Hence it was thought that the best results were those got by noting the change of Curie point following a change of pressure. For this reason the abscissa zero represents the initial pressure, whatever that might be. For example, if the initial pressure were 4000 atmos, a change to 6000 atmos would be recorded as +2000 atmos and the corresponding Curie-point change noted. If the pressure were then reduced from 6000 to 2000 atmos, the pressure change would be recorded as −4000 atmos.

It will be noticed that there is considerable scatter of the experimental results for all samples for which the gas system was used. In all cases the change of Curie point is of the same order of magnitude as the experimental error. There is also additional uncertainty in the thermocouple readings because these high temperatures go beyond the range of the thermocouple calibration for the pressure effect. However, the results seem to indicate that the change is very much smaller than that predicted for Fe by Kornetzki or for Co by Néel.

Table I lists the change per 1000 atmos of all samples with an estimate of the experimental error based on the scatter in Figs. 9 and 10. This assumes a linear change of Curie point with pressure and does not include any error resulting from the effect of pressure on the thermocouple. More detailed information on the probable error can be obtained from the curves of output *vs* temperature for each sample at different pressures, but these are not reproduced here because of space limitations.

TABLE I. Change of Curie point with pressure.

Sample	Approx Curie temp	Deg change per 1000 atmos (+ indicates increase)	Predicted change
Fe	770°C	0 ±0.1	+0.79[a]
			−5 to −10[b]
Co	1120°	0 ±1	−4.6[a]
Ni	360°	+0.35±0.02	−0.13[a]
			+0.05[c]
			+0.35[d]
Gd	16°	−1.2 ±0.05	
96Fe 4Si	733°	−0.1 ±0.1	
90Fe 10Si	615°	+0.2 ±0.2	
Compensator 70Fe 30Ni	80°	−5.8 ±0.2	−5[b]
Invar 64Fe 36Ni	210°	−3.6 ±0.1	
Permalloy 68Ni 32Fe	606°	−0.1 ±0.1	
Monel	50°	+0.07±0.03	+0.06[e]
Alumel 94Ni	143°	+0.04±0.02	
$Mn_{\frac{1}{2}}Zn_{\frac{1}{2}}Fe_2O_4$	90°	+0.9 ±0.04	
$La_{0.75}Sr_{0.25}MnO_3$	80°	+0.6 ±0.04	

[a] See reference 6.
[b] See reference 11.
[c] See reference 13.
[d] See reference 12.
[e] See reference 9.

Chemical Analysis of Samples

The Fe and Co were high purity samples obtained from the Institute's metallurgy section, and the Ni was a high purity sample (>99.9 percent) obtained from the Bell Telephone Laboratories. The Gd was prepared by A. Moskowitz under the direction of Dr. N. H. Nachtrieb, and the largest impurity shown by spectroscopic analysis was 0.1 percent Fe.

No chemical analysis was obtained for the commercial alloys Monel, Alumel, Invar, and Permalloy. The percentages shown in Table I are the usual percentages for these alloys.

The FeSi alloys reported as 96Fe 4Si and 90Fe 10Si were found to have 3.5 percent and 10.5 percent, respectively of Si. The ferrite was found to be represented approximately by the formula $Mn_{\frac{1}{2}}Zn_{\frac{1}{2}}Fe_2O_4$ (the Mn was 3 percent short, and the Zn was 5 percent short). The Compensator alloy contained 29.7 percent Ni. The formula $La_{0.75}Sr_{0.25}MnO_3$ represents the proportions which went into the preparation of this sample—no analysis was made subsequently.

Discussion of Results

Fe and Fe-Si Alloys

Fe is of special interest because of the decrease of Curie point with pressure of 5 to 10 deg per 1000 atmos predicted by Kornetzki, using volume magnetostriction measurements made between 20°C and 100°C. Smoluchowski[19] has also treated this problem, and he calculated the volume dependence of the Weiss constant from the same data. His calculations are $N^{-1}dN/d\omega = 44.1$ at 20°C and $N^{-1}dN/d\omega = 32.2$ at 100°C, a marked decrease with rising temperature. If one takes the point of view that interatomic distance D is the important factor and that the decrease of volume dependence with temperature is due to thermal expansion, then the conclusion is that the interaction curve rises sharply at the room temperature value of D in Fe but has reached the top of the curve at 770°C, for which D is about 1 percent greater—hence no change of Curie point with pressure in the present experiment. If this is so, a large decrease of Curie temperature could be obtained with a pressure of 50 000 atmos, which would reduce the lattice constant to its room temperature value.

Because 50 000 atmos is not available, the experiment was carried out on two Fe-Si alloys. Si reduces the lattice parameter of Fe and magnetically appears to act as a diluent, leaving the magnetic moment of the Fe atom unchanged up to about 5-percent Si by weight. The Curie point is lowered, and the combination of reduced D and lower Curie point results in a value of D

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[19] R. Smoluchowski, Phys. Rev. **59**, 309 (1941); R. Smoluchowski, Phys. Rev. **60**, 249 (1941).

at the Curie point of the 10-percent Si alloy which is very nearly that of pure Fe at 20°C. If interatomic distance is the important parameter in magnetic interaction, a large decrease of Curie point with pressure should have been observed in the 10-percent Si alloy, in view of the volume dependence shown by the magnetostriction data.

Cobalt

The result for Co (no change with pressure) is in contradiction to the prediction of Néel (a decrease of 4.6° per 1000 atmos). However, the temperature of 1120°C is far beyond the 580°C to which the pressure calibration of the thermocouple was carried; therefore, the result cannot be regarded with the same certainty as those for the other samples.

Nickel

Although here again the result differs from Néel's prediction, there is rough agreement with predictions based on the volume magnetostriction and on the thermal expansion anomaly. Ni satisfies all the requirements for good experimental accuracy. The Curie temperature is low enough so that the liquid system may be used, the drop in output occurs within 2°, and there is no significant change in permeability under pressure. Figure 11 shows the output curves for several pressures.

Gadolinium

For this element the generalized interaction curves must predict an increase with pressure rather than the observed decrease. The inner incomplete shell is in this case the $4f$ shell with 7 electrons (a half-filled shell), and its small size results in a greater ratio of D/d and a greater value of $D-d$ than for any of the transition metals Fe, Co, or Ni.

Compensator Alloy

This is similar to the alloy which Steinberger reported as becoming paramagnetic under pressure (at room temperature). Kornetzki also predicted a decrease of about 5° per 1000 atmos from volume magnetostriction measurements, which agrees with the results found here.

Some doubts about the effect of phase change in this system had been expressed.[20] However the changes with pressure were found to be instantaneous and reversible and proportional to the applied pressure; hence, a phase change cannot be responsible. X-ray powder pictures showed that the sample was in the 2-phase region; the amount of body-centered (α) phase was estimated to be about 5 or 10 percent.

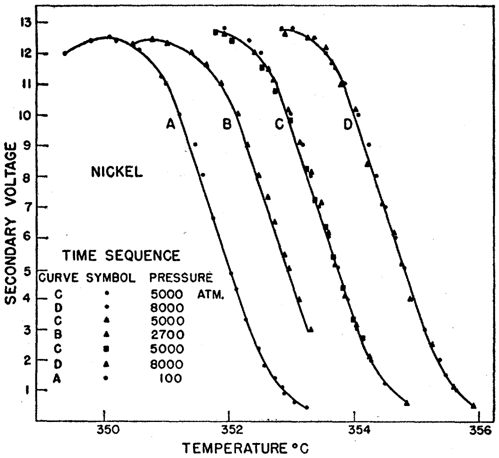

FIG. 11. Secondary voltage *vs* temperature for Ni at several pressures.

Invar

This alloy is close to Compensator in composition but is a single phase alloy (f.c.c.). The decrease of Curie point with pressure is smaller but of the same order of magnitude. The very abnormal thermal expansion gives a good indication of the result to be expected.

Permalloy

This is another Fe-Ni alloy, but one of the composition having scarcely any thermal expansion anomaly. Hence the negligible change of Curie point with pressure was to be expected.

Monel

The change here is in agreement with that found by Michels *et al.*

$La_{0.75}Sr_{0.25}MnO_3$

For this ceramic-type material (perovskite crystal structure) Zener[21] has proposed a formula relating conductivity and Curie point. It would therefore be interesting to compare change of Curie point with change of conductivity under pressure. However, the formula applies only in the temperature range in which the conductivity is metallic, which would be at low temperatures in this case since the material is a semiconductor at room temperature.

V. CONCLUSIONS

The generalized interaction curves shown in Figs. 2 and 3 are not consistent with the results of this experiment. Apart from the objection to plotting the Curie point in Fig. 2 which was mentioned earlier, this curve would predict an increase of Curie point for Gd instead of a decrease, a large decrease for Fe instead of no change, and a larger increase for Ni than was observed.

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[20] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951), p. 726.

[21] C. Zener, Phys. Rev. **82**, 403 (1951).

Néel's predictions for Fe, Co, and Ni are not confirmed. Figure 3 does not include Gd, but if the same rules had been used for placing it on the curve, Fig. 3 would also predict an increase. In fact, the only element for which both curves would predict the same direction of the change would be Gd, and the predicted change would be wrong.

The Forrer correlation would lead one to expect much larger changes than are observed. This suggests that the ferromagnetic range may be much wider than 10 percent of D in metals and that the conduction electrons may play a role in the interaction, as outlined by Zener. If this is so, it explains the failure of the generalized interaction curves also, as they would then be omitting an important parameter. The results on Fe and the Fe-Si alloys also tend to show that interatomic distance is not an all-important parameter.

One may still suppose that the interaction curve for a single element takes the form of Fig. 1. The fact that some large decreases of Curie point with pressure have been found but no large increases suggests that there may be a steep rise of the interaction curve as it crosses over from the antiferromagnetic region but only a gradual fall at large D. This is supported by the fact that there are no large values of negative volume magnetostriction reported nor large positive thermal expansion anomalies.

VI. ACKNOWLEDGMENTS

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The Influence of Pressure on the Curie Temperature of Iron and Nickel*

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A comparison is made between Patrick's measurements of the change of Curie temperature under pressure and theory based on a Brillouin function. The agreement is fair.

The usual assumption in the molecular-field theory of magnetism is that the saturation magnetization at absolute zero is independent of volume. An alternate procedure[1,2] based on the Brillouin function and on experimental volume magnetostriction data gives explicit values for N, the volume dependent field constant, and for I_0, the volume dependent saturation magnetization at absolute zero. The agreement with experimental data such as specific heat and with some magnetocaloric effects is satisfactory for coupled pairs of spins ($j=1$). Up until now there were no data available for comparing the predicted influence of pressure on the Curie temperature with experiments. The recent very interesting results obtained by Patrick[3] make such a comparison between experiment and theory possible.

This comparison can be made in several ways depending upon which of the necessary extrapolations seems to be most reliable. One of them is to use the formula

$$\frac{1}{\theta}\frac{\partial\theta}{\partial\omega}=\frac{1}{N}\frac{\partial N}{\partial\omega}+\frac{1}{I_0}\frac{\partial I_0}{\partial\omega}, \tag{1}$$

in which $\partial\omega$ is the relative change of volume dV/V. Using, in the right side of (1), the values (for $j=1$) given in reference 2, one obtains -1.7 at room temperature for nickel and $+21.2$ at 100°C for iron. These are the highest temperatures for which volume magnetostriction data are available. Since compressibility at the Curie points is not known, one has to use room temperature values which give for the relative decrease of volume at 1000-atmos pressure 0.55×10^{-3} and 0.6×10^{-3} for nickel and iron, respectively. One obtains thus for the change of the Curie temperature of nickel the value $+0.57$ deg and the value -13.3 deg for iron as compared with the observed $+0.35\pm0.03$ and 0 ± 0.2, respectively. The comparison for nickel, in view of the many assumptions and extrapolations, is fair whereas for iron it appears to be off by two orders of magnitude. It should be observed, however, that the above calcu-

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[1] R. Smoluchowski, Phys. Rev. **59**, 309 (1941).

[2] R. Smoluchowski, Phys. Rev. **60**, 249 (1941).

[3] L. Patrick, this issue [Phys. Rev. **93**, 384 (1954)].