constant is 22.3 Cal. As far as the lattice constant goes, one must remember, however, that both the correlation energy and that due to the Fermi hole are calculated for a flat wave function and the wave functions are flat only for $r_s=4$ and its neighborhood.

The magnitude of the correlation energy is important for questions of paramagnetism and ferromagnetism as well as for questions of lattice energy. It modifies Bloch's original theory on the ferromagnetism of free electrons[11] in such a way that it yields ferromagnetism in fewer cases than in its original form.[12] I hope to return to this question at another time.

I wish to express my gratitude to Dr. F. Seitz for his kind help in connection with the preparation of this manuscript.

[12] A paper of S. Schubin and S. Wonsowsky, Proc. Roy. Soc. **A145**, 159 (1934) which appeared recently, points in the same direction.

DECEMBER 1, 1934 PHYSICAL REVIEW VOLUME 46

Thermal Expansion and the Ferromagnetic Change in Volume of Nickel

CLARKE WILLIAMS, *Columbia University*

(Received October 11, 1934)

The coefficient of thermal expansion is measured at intervals of 2.5°C between 200°C and 500°C for single and polycrystalline specimens of nickel of varying known degrees of purity. The data yield the value $3.24\pm0.15\times10^{-4}$ for the ferromagnetic change in volume per unit volume of pure nickel.

INTRODUCTION

WHEN the coefficient of thermal expansion of nickel is plotted as a function of temperature the resulting graph has a hump which starts at about 200°C and terminates in the neighborhood of the Curie point. The area under the graph represents a change of length (and hence of volume), and the area under the hump may properly be taken as a measure of the change in volume associated with those interatomic forces (or energies) in terms of which the ferromagnetism of the material finds its explanation. Fowler and Kapitza[1] were the first to point out that Heisenberg's theory of ferromagnetism is competent to offer a quantitative description of this phenomenon. Their calculation has been extended by Powell,[2] who obtained an expression relating the change in volume per unit volume to the exchange energy between pairs of electrons belonging to neighboring atoms. The observations upon which Powell based his numerical estimate of the former quantity were obtained by Colby,[3] who worked with polycrystalline nickel of unspecified purity. It seemed worth while to repeat Colby's measurements upon single and polycrystalline nickel of varying known degrees of purity, and to extend them over a greater range of temperature in order to increase the precision of the base line from which the hump is reckoned. The present paper is a report based upon these experiments.

APPARATUS AND METHOD

The dilatometer (Fig. 1) is constructed entirely of fused quartz. A knife edge, A, and a table, B, rest upon a flat plate, C. The top of the table is ground flat and polished, and carries a ground roller about 1 mm in diameter. The specimen, S, is a circular cylinder about 5 mm in diameter and 6 cm to 7 cm long. A tiny lateral scratch is made near one end and the other end is polished. The scratch engages the knife edge and the polished end rests on the roller. Mirrors M_2 and M_4, of gold sputtered on quartz, are fused to the ends of the roller. These mirrors are rotated slightly with

[1] Fowler and Kapitza, Proc. Roy. Soc. **A124**, 1 (1929).
[2] Powell, Proc. Phys. Soc. **42**, 390 (1930).
[3] Colby, Phys. Rev. **30**, 506 (1910).

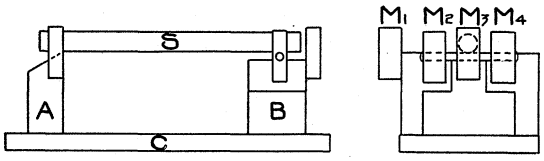

FIG. 1. The quartz dilatometer.

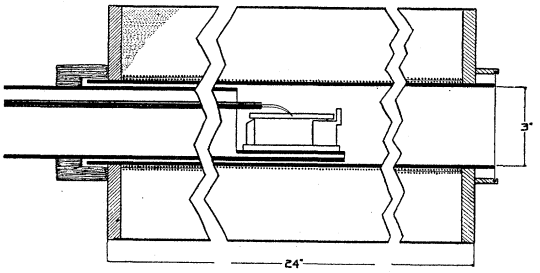

FIG. 2. The dilatometer and furnace assembly.

respect to each other about the roller axis to increase the range of the instrument. A mirror, M_1, is fused to the knife edge, and another, M_3, to the table.

Fig. 2 is a diagram of the dilatometer and furnace assembly. The dilatometer rests in the center of the furnace on a quartz plate fused to one end of a quartz tube 2.5 inches in diameter and 2 feet long. The other end of this tube is held in a mounting insulated against building vibration. The heating element of the furnace is a bifilar winding of No. 18 Constantan wire on a quartz tube 3 inches in diameter and 26 inches long, together with an auxiliary winding over a length of 6 inches at each end. The open end of the furnace is closed with a microscope cover glass.

The junction of a platinum *vs.* platinum—10 percent rhodium thermocouple nearly touches the specimen at its center. The thermal e.m.f. is measured with a Leeds and Northrup Type K potentiometer.

The mirrors are so aligned that they reflect into a theodolite light from four vertical scales, one for each mirror. The scales are four meters from the dilatometer, and can be independently illuminated. Readings on the scales associated with mirrors M_1 and M_3 reveal any rotation of the dilatometer as a whole.

Prior to each set of observations the specimen is demagnetized in an alternating magnetic field, mounted in the dilatometer, and carried through several cycles of heating and cooling over the temperature range 300°C to 400°C. Thermal equilibrium is then established and observations are made at 5° intervals over a complete cycle of heating and cooling. The initial temperature is then altered 2.5 degrees and the procedure repeated. The data thus yield mean values of the coefficient of thermal expansion over 5° intervals corresponding to mean temperatures which differ by 2.5°.

RESULTS

Observations are here reported upon five different specimens of nickel, namely:

I. A single crystal of Mond nickel grown in an atmosphere of hydrogen at a pressure of about 1 mm;[4]

II. A single crystal grown of nickel purified in the manner described by Fink and Rohrman,[5] but contaminated with carbon, and with molybdenum from the winding of the furnace in which the crystal is grown;

III. A polycrystalline specimen of the same material as II, but containing more molybdenum;

IV. A specimen of hard drawn commercial nickel;

V. Specimen IV, annealed 1 hr. in hydrogen at 1100°C and cooled slowly.

Table I shows the purity of the several specimens. The analysis of specimen IV was supplied by the International Nickel Co. The carbon content of specimen III was determined chemically by Dr. L. A. Wooten, of the Bell Telephone Laboratories. The remainder of the data represent quantitative spectroscopic analyses made by Lucius Pitkin, Inc. of New York.

Laue photographs taken through thin sections sawn from the ends of specimens I and II indicate that the orientations of the respective

TABLE I. *Percent impurity in specimens.*

	I	II	III	IV
Mo	0.075	0.5–0.6	0.75–0.9	0.11
C	0.02–0.06	0.06–0.1	0.05–0.09	0.3–0.4
Co	*	*	*	0.13
Cu	0.01–0.02	0.005–0.01	0.001–0.005	0.41
Fe	0.001–0.005	0.005–0.01	0.01–0.02	
Mg	trace	trace	trace	
Mn	*	*	*	0.02
Al	*	*	*	
Si	trace	trace	trace	0.09
Sn	*	trace	trace	

* Not found.

[4] Dingwall, Zacharias and Siegel, Trans. Electrochem. Soc. **63**, 395 (1933).

[5] Fink and Rohrman, Trans. Electrochem. Soc. **57**, 325 (1930); **58**, 403 (1930); **59**, 359 (1931).

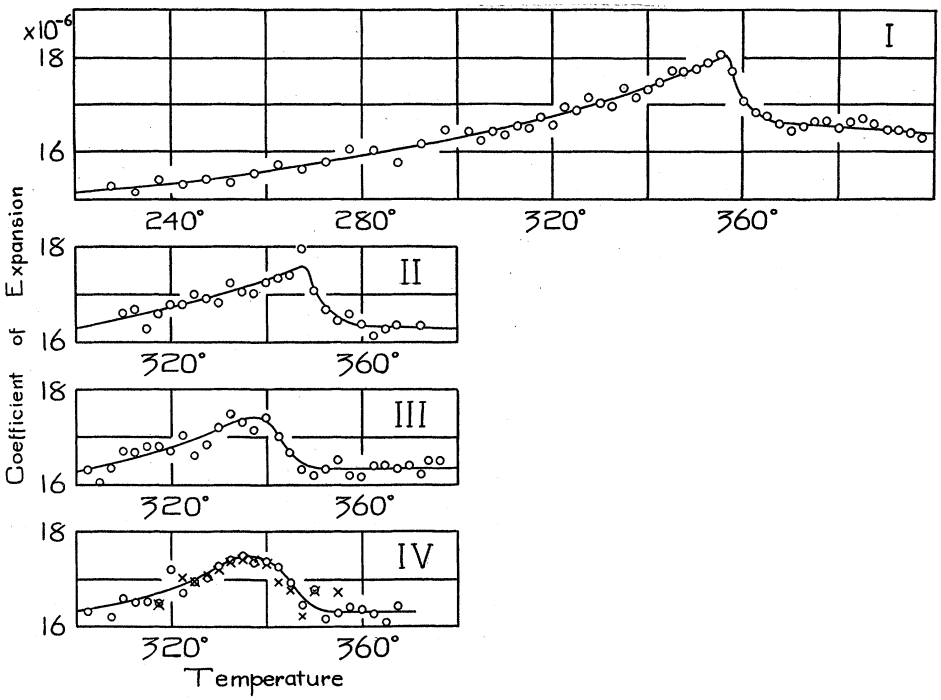

FIG. 3. Variation of coefficient of thermal expansion with temperature for various specimens of nickel.

cylinder axes relative to the crystal axes are quite dissimilar.

The data obtained with the several specimens are shown graphically in Fig. 3. The crosses on curve IV represent observations made on specimen V. Each point in the range 320°–380° represents the mean of four to six observations. All the observations are corrected for the expansion of the quartz dilatometer.

It is to be noted that there is no evidence of hysteresis in this phenomenon; the heating and cooling curves are indistinguishable. Again, the annealing process to which specimen IV was subjected leaves the phenomenon unaltered. Rough measurements of the magnetization as a function of temperature in specimen I indicate that the Curie point of this material is in the neighborhood of 370°C.

PRECISION

The sources of systematic error in these measurements are (1), errors in measurement of the specimen length and of the quantities which determine the dilatometer magnification; (2), a longitudinal temperature gradient in the furnace; (3), the thermocouple calibration; and (4), a difference in temperature between the thermocouple junction and the specimen.

The distance between the roller and knife edge is measured with a travelling microscope to 0.1 percent, and the dilatometer magnification to 0.2 percent. The maximum allowed temperature gradient near the center of the furnace,measured with the specimen removed, is 0.13°C per cm. Accordingly, the actual temperature of the specimen must be uniform to better than 0.5°C. The thermocouple calibration used is that given by the Bureau of Standards.[6] This is checked and the remaining sources of error estimated by replacing the specimen with a glass encased Leeds and Northrup platinum resistance thermometer calibrated by the Bureau of Standards. Under these circumstances the maximum discrepancy between the two thermometers over a period of eighteen months was 0.8°C in the range 300°–400°. Furthermore, the 5° intervals as

[6] Bur. Standards J. Research **10**, 280 (1933).

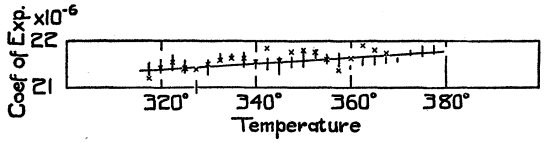

FIG. 4. Illustrating the behavior of the dilatometer. The substance is fine silver.

measured by the two thermometers agree to better than 0.09°C.

The magnitude of the accidental errors inherent in the method are exhibited in Fig. 4, which depicts the result of a series of measurements on a bar of fine silver. The lengths of the lines indicate twice the mean deviation of four sets of observations. The crosses show the mean values of two sets of observations taken after the dilatometer had been completely dismantled and reassembled.

THE FERROMAGNETIC CHANGE OF VOLUME

An evaluation of the ferromagnetic change in length requires an authentic base line from which to calculate the area under the hump. This is secured by combining the data obtained in these experiments with those reported by Hidnert.[7] Hidnert worked with a specimen of electrolytic nickel which contained 0.03 percent iron and 0.03 percent of other metallic impurity, and reported mean values of the thermal expansion coefficient over temperature intervals of 100°C between 100°C and 900°C.

Fig. 5 is a graph of the composite data. The crosses indicate Hidnert's values and the circles in the temperature range 400°–500° indicate values obtained in these experiments. The humps are reproductions, on the altered scale, of curves I and II of Fig. 3. With the exception of the single observation of Hidnert over the range 400°–500°, the data are in excellent accord, and yield a fairly satisfactory base line shown by the dotted portion of the curve. It appears that 0.6 percent or less of impurity leaves the base line

[7] Hidnert, Bur. Standards J. Research 5, 1305 (1930).

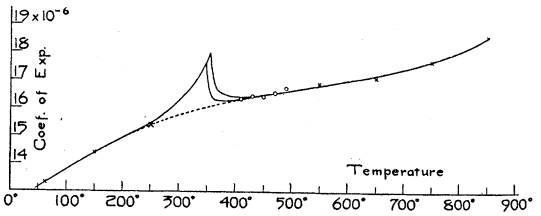

FIG. 5. The base line for measuring the ferromagnetic change in length. The humps are curves I and II of Fig. 3.

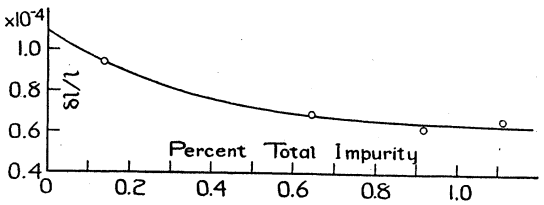

FIG. 6. Variation of the ferromagnetic change in length with total impurity for nickel.

and ascending part of the hump unaltered, and that the value of the change in length per unit length diminishes with increasing amount of impurity. Accordingly it is suggested that the value of the ferromagnetic change in length for pure nickel be obtained by extrapolation.

Fig. 6 is a curve for which the ordinates of the plotted points are the areas under the four curves of Fig. 3 with respect to the base line shown in Fig. 5, while the abscissae are the percentages of total impurity as given in Table I. The extrapolated value of the ferromagnetic change in length per unit length for pure nickel is

$$1.08 \pm 0.05 \times 10^{-4}.$$

The precision measure is obtained from the uncertainty in the total impurity as given in Table I.

In conclusion the author desires to express his thanks to the Physics Department of Columbia University for the facilities placed at his disposal to Dr. L. A. Wooten for the determination of the carbon content of specimen III, and to Dr. S. L. Quimby, who suggested the problem and followed the progress of its solution with helpful counsel and encouragement.