

in procedure. In the crudest approximation all these theories give the same answer. However, it is felt that the theory of Bogoliubov is more fundamental since it is derived from the variational point of view.

*Note added in proof.* In the present discussion the electron-phonon interaction is assumed to be so weak that a second-order perturbation calculation is adequate. When the interaction is strong, the method of Eliashberg allows, in principle, a summation to all

orders of perturbation. On the other hand there exists no extension of Bogoliubov method for the strong coupling case.

#### ACKNOWLEDGMENTS

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### Specific Heat of Ferrites at Liquid Helium Temperatures\*†

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The specific heat of lithium, cobalt, magnesium, and nickel ferrite has been measured from 1.8°K to 5°K using a calorimetric technique similar to that used by Clement. A "heat switch" was used to cool the samples rather than a helium exchange gas, thereby avoiding helium desorption effects. In all cases the specific heat  $C$  could be described by the relation  $C = \alpha_M T^{\frac{3}{2}} + \beta T^3$ , where  $T$  is the temperature and  $\alpha_M$  and  $\beta$  are constants. The Debye temperatures were computed from  $\beta$  and were in good agreement with values obtained at liquid nitrogen temperatures. The  $T^{\frac{3}{2}}$  temperature dependence verifies the spin-wave theory for these compounds although the values of  $\alpha_M$  were consistently larger than anticipated from observed values of the Curie temperatures. Possible explanations for this are discussed. An extra term proportional to  $T^{-2}$  was observed for cobalt ferrite and this was identified as the nuclear contribution to the specific heat. From the magnitude of this term the magnetic field at the nucleus of the cobalt ion was evaluated and found to be approximately 410 koe.

#### I. INTRODUCTION

SPIN-WAVE theory<sup>1,2</sup> predicts that for a ferromagnetic or a ferrimagnetic material there should be a contribution to the specific heat which is proportional to the temperature to the three-halves power. Measurements, by Kouvel,<sup>3</sup> of the temperature dependence of the specific heat of the ferrite  $\text{Fe}_3\text{O}_4$  indicated the presence of this term. This work constituted one of the first direct verifications of the spin-wave theory. It was, however, pointed by Kouvel that the exchange parameters obtained by low-temperature specific heat measurements did not agree with high-temperature measurements of the same parameters.

The temperature dependence of the specific heat has been measured for a wide class of ferrites, among which are nickel, magnesium, lithium, and cobalt ferrites, in order (a) to test the  $T^{\frac{3}{2}}$  law over a wide range of ferrites

and (b) to evaluate exchange parameters from low-temperature data.

In all the samples measured, the  $T^{\frac{3}{2}}$  dependence of the spin-wave specific heat was observed. However, its magnitude was, as with the results of Kouvel, larger than anticipated from high-temperature determinations of the exchange integral.

#### II. THEORY

We now evaluate the specific heat in a ferrite in the absence of a dc applied magnetic field. We will consider the effects of exchange interactions and the interactions between the spins and the dipole field.

Kittel and Herring<sup>4</sup> have shown that the dispersion relation for spin waves under these assumptions and in a medium of high symmetry can be written

$$\omega^2(K) = (\eta K^2)(\eta K^2 + 4\pi M_s \gamma \sin^2 \theta_K), \quad (1)$$

where  $\eta = (A/M_s)(ge/mc)$ ,  $A$  is the Landau-Lifshitz<sup>5</sup> exchange constant,  $M_s$  is the saturation magnetization,  $\gamma = e/mc$ ,  $g$  is the spectroscopic splitting factor, and  $\theta_K$  is the angle between the direction of propagation of a spin wave and the easy direction of magnetization.

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<sup>1</sup> J. S. Kouvel and J. Brooks, Technical Report No. 198, Cruft Laboratory, Harvard University, 1954 (unpublished).

<sup>2</sup> J. S. Kouvel, Technical Report No. 210, Cruft Laboratory, Harvard University, 1955 (unpublished).

<sup>3</sup> J. S. Kouvel, Phys. Rev. **102**, 1489 (1956).

<sup>4</sup> C. Herring and C. Kittel, Phys. Rev. **81**, 869 (1951).

<sup>5</sup> L. Landau and E. Lifshitz, Physik. Z. Sowjetunion **8**, 153 (1935).

TABLE I. Specific heat parameters.

Material	$g_{\frac{1}{2}}$	$g_{\frac{3}{2}}$	$\delta$	$10^5\lambda$
CoFe <sub>2</sub> O <sub>4</sub>	1.170	1.709	1.275	9.874
NiFe <sub>2</sub> O <sub>4</sub>	1.236	1.899	1.309	7.750
MgFe <sub>2</sub> O <sub>4</sub>	1.288	2.093	1.326	3.916
Li <sub>0.5</sub> Fe <sub>2.5</sub> O <sub>4</sub>	1.236	1.899	1.309	8.160
Ni <sub>0.88</sub> Fe <sub>2.12</sub> O <sub>4</sub>	1.230	1.880	1.306	8.393
Ni <sub>0.68</sub> Fe <sub>2.42</sub> O <sub>4</sub>	1.192	1.791	1.290	8.726

Above 2°K,  $\eta K^2$  is at least five times larger than  $4\pi\bar{M}_s\gamma$  so that we can expand Eq. (1) and, keeping terms to first order in  $\bar{M}_s$  we get

$$\omega(K) = \eta K^2 + 2\pi\bar{M}_s\gamma \sin^2\theta_K. \quad (2)$$

In terms of  $\omega(K)$ , the free energy  $F$  can be written as

$$F = -kT \sum_K \ln[1 - \exp(-\hbar\omega(K)/kT)]. \quad (3)$$

In a fashion identical to that of Galt, Kunzler, and Walker,<sup>6</sup> Eq. (3) leads to a specific heat correct to first order in  $\bar{M}_s/T$ , given by

$$C = -\frac{k}{8} \left( \frac{kT}{\pi\hbar\eta} \right)^{\frac{3}{2}} \left[ \frac{15}{4} g_{\frac{1}{2}} \left( \frac{2\bar{M}_s}{3T} \right) + \frac{2\bar{M}_s}{T} g_{\frac{3}{2}} \left( \frac{2\bar{M}_s}{3T} \right) \right], \quad (4)$$

where  $\bar{M}_s = (2\pi\hbar\gamma/k)M_s$  and the function  $g$  is given by

$$g_i(\rho) = \sum_{n=1}^{\infty} \frac{1}{n^i} \exp(-\rho n).$$

Curves of  $g_{\frac{1}{2}}(2\bar{M}_s/3T)$  and  $g_{\frac{3}{2}}(2\bar{M}_s/3T)$  versus  $T$  are shown in Fig. 1. Since  $g_{\frac{1}{2}}$  is very weakly temperature dependent and since the coefficient of  $g_{\frac{1}{2}}$  is between 0.03 and 0.07 (depending upon the particular ferrite) we will treat them both as constants and use their value at  $T = 3.5^\circ\text{K}$  (the mean temperature of our measurements). Letting  $\delta = g_{\frac{1}{2}} + (8/15)(\bar{M}_s/T)g_{\frac{3}{2}}$ , Eq. (4) can then be written as

$$C = -\frac{k}{8} \left( \frac{kT}{\pi\hbar\eta} \right)^{\frac{3}{2}} \frac{15}{4} \delta. \quad (5)$$

The values of  $g_{\frac{1}{2}}(2\bar{M}_s/3T)$ ,  $g_{\frac{3}{2}}(2\bar{M}_s/3T)$ , and  $\delta$  are shown in Table I for the ferrites measured in this experiment. We then have that dipole interactions do not alter the  $T^{\frac{3}{2}}$  temperature dependence for the spin wave specific heat above 1.5°K. Multiplying Eq. (5) by the molecular weight (M.W.) divided by the density  $\rho$  will then give the magnon specific heat per mole. Equation (5) then becomes

$$C = -\frac{k}{8} \left( \frac{k}{\pi\hbar\eta} \right)^{\frac{3}{2}} \frac{15}{4} \frac{\text{M.W.}}{\rho} T^{\frac{3}{2}} = \alpha_M T^{\frac{3}{2}}. \quad (6)$$

In terms of  $\alpha_M$ , the Landau-Lifshitz exchange constant

<sup>6</sup> J. K. Galt, J. E. Kunzler, and L. R. Walker, Phys. Rev. **119**, 1609 (1960).

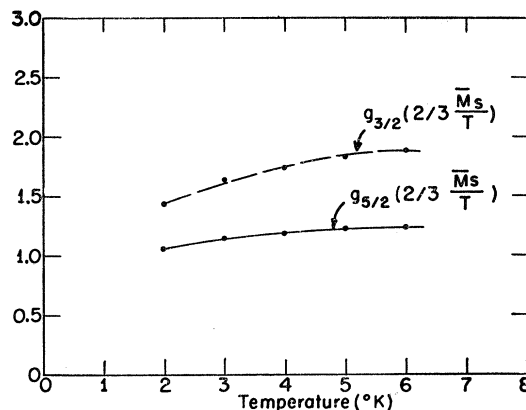


FIG. 1.  $g_{\frac{1}{2}}(2\bar{M}_s/3T)$  and  $g_{\frac{3}{2}}(2\bar{M}_s/3T)$  versus temperature for cobalt ferrite.

can be written as

$$A = \frac{M_s}{ge/mc} \frac{k}{\hbar\pi} \left( \frac{15k \text{ M.W.}}{32\rho} \delta \right)^{\frac{3}{2}} \frac{1}{\alpha_M^{\frac{3}{2}}},$$

or

$$A = \lambda / \alpha_M^{\frac{3}{2}}. \quad (7)$$

The value of  $\lambda$  when  $\alpha_M$  is expressed in ergs/mole( $^\circ\text{K}$ ) <sup>$\frac{3}{2}$</sup>  is also shown in Table I for the ferrites measured.

Since the Debye theory predicts a  $T^3$  temperature dependence for the phonon specific heat, the total specific heat of ferrites at low temperatures can be given by the relation,

$$C = \alpha_M T^{\frac{3}{2}} + \beta T^3, \quad (8)$$

where for ferrites,

$$\beta = (1.361 \times 10^4 / \Theta_D^3) \text{ joules/mole } (^\circ\text{K})^4, \quad (9)$$

and  $\Theta_D$  is the Debye characteristic temperature. There should be no electronic contribution to the specific heat of a ferrite. Kouvel has also shown<sup>1,2</sup> that  $\alpha_M$  can, to within 15%, be given by the expression

$$\alpha_M = 0.226R \left\{ \frac{[(S_{B1} + S_{B2}) - S_A]K}{4J_{AB}S_A(S_{B1} + S_{B2})} \right\}^{\frac{3}{2}}, \quad (10)$$

where  $R$  is the universal gas constant,  $S_{B1}$  and  $S_{B2}$  are the spins on the  $B$  site,  $S_A$  is spin on the  $A$  site, and  $J_{AB}$  is the  $A$ - $B$  exchange integral and is related to the Curie temperature  $T_c$  through the equation,

$$J_{AB} = \frac{kT_c}{4[2S_A(S_A + 1)S_B(S_B + 1)]^{\frac{1}{2}}}, \quad (11)$$

where  $S_B$  is the average spin on the  $B$  site. In terms of Eqs. (7), (9), and (10), the Landau-Lifshitz exchange constant, the exchange integral  $J_{AB}$ , and the Curie temperature can be evaluated once  $\alpha_M$  is determined.

## III. DESCRIPTION OF SAMPLES

The samples were sintered from commercial chemicals.<sup>7</sup> Their densities ranged from 89% to 93% of x-ray densities. All the samples were x-rayed and chemically analyzed for major metallic content and the average grain size was measured. These results are shown in Table II. The samples were also analyzed for zinc content and were found to contain approximately 0.02% zinc. This was done to eliminate the possibility of a low-temperature phase transition which would have affected the measurements taken over the temperature range covered in this experiment.

The samples were supplied in the shape of cylinders and there were two of each. Each cylinder was mounted in a magnetic chuck and the flat surfaces were milled parallel. A channel was cut in each cylinder as shown in Fig. 2 which was large enough to fit one half of a  $\frac{1}{4}$ -watt carbon resistor. Three holes approximately 1 mm in diameter were cut in one of the two cylinders and were used to support the samples in the calorimeter. The channel and holes were cut with an S. S. White abrasive cutter. The samples were then cleaned in an Alcar Instruments Ultrasonic Cleaner in an acetone bath, dried and weighed to within  $\pm 0.001$  g. Their weights are also given in Table II.

A pre-weighed carbon resistor with leads was placed in the channel of one of the cylinders and covered with a thin coating of Glyptal. The other cylinder, with about 4 mg of Glyptal on its surface, was placed on top of the first, such that the resistor fit tightly in the channels. This combination was then baked at 80°C for 8 hr, after which the sample was again weighed. In this way the amount of Glyptal used to cement the sample together could be determined. The sample was then ready for measurement.

## IV. EXPERIMENTAL

Data were taken using a technique similar to that used by Clement and Quinell.<sup>8</sup> The sample was heated at approximately 0.3 mdeg/sec with a heat input of approximately 1 to 9 ergs/sec depending upon the temperature at which the measurement was made.

This small heat input to the sample required extremely good thermal isolation between the sample and the bath. By taking all the data between the hours of 10:30 p.m. to 6:30 a.m., the vibrational heating of the sample was kept to a minimum, and by continuously adjusting the bath temperature to follow the sample temperature, the total heat exchange between the sample and the helium bath was kept to within  $\pm 0.2$  erg/sec.

The sample was heated for alternate 5-min periods and during the heating period the temperature was measured ten times (approximately every 30 sec). Temperature measurements were made with a 75-ohm  $\frac{1}{4}$ -watt Allen-Bradley carbon-composition resistor which formed one arm of a three-lead Wheatstone bridge. The bridge output was detected with a Beckman model 14 dc amplifier, which in turn drove an L and N recorder. The resistor was cemented at the center of the sample (see Sec. III) and it also served as the heater. The resistor was calibrated against the vapor pressure of the liquid helium bath (using the  $TL_{55}$  vapor pressure scale) after all measurements were made.

A computer program was written for a Univac which fitted the resistance-temperature, calibration points to the equation,

$$[(\log R)/T]^{\frac{1}{2}} = a + b \log R. \quad (12)$$

The computer gave the values of  $a$  and  $b$ , and with this equation the temperature of any calibration point could be reproduced to within  $\pm 0.001^\circ\text{K}$ . The equation was then solved for  $T$  as a function of  $R$  so that for each resistance measurement the temperature could also be evaluated by the computer. By measuring the time between resistance measurements we thereby obtain 10 time-temperature points for each 5-min heating cycle. The computer then fitted this to a curve (straight line) and computed the slope at the center of each heating cycle and evaluated the initial and final temperature of each cycle. With these, we could then determine the heat capacity of the sample (see reference 8). By subtracting the heat capacity of the resistor, leads, and Glyptal, calculated from previously measured

TABLE II. Properties of samples.

Sample	Percent composition	Chemical formula	X-ray lattice parameter (Å)	Average grain size (mm)	Sample weight (moles)
NiFe <sub>2</sub> O <sub>4</sub>	Ni: 23.53%; Fe: 48.80%	Ni <sub>0.94</sub> Fe <sub>2.06</sub> O <sub>4</sub>	8.339	0.12	0.3025
MgFe <sub>2</sub> O <sub>4</sub>	Mg: 9.79%; Fe: 58.43%	Mg <sub>0.82</sub> Fe <sub>2.18</sub> O <sub>4</sub>	8.362	0.1	0.332
CoFe <sub>2</sub> O <sub>4</sub>	Co: 20.12%; Fe: 50.27%	Co <sub>0.83</sub> Fe <sub>2.17</sub> O <sub>4</sub>	8.390	2.0	0.2345
			(Ordered)		
Li <sub>0.5</sub> Fe <sub>2.5</sub> O <sub>4</sub>	Li: 1.71%; Fe: 67.20%	Li <sub>0.5</sub> Fe <sub>2.50</sub> O <sub>4</sub>	8.338	0.3	0.246
Ni <sub>0.8</sub> Fe <sub>2.2</sub> O <sub>4</sub>	Ni: 22.02%; Fe: 50.14%	Ni <sub>0.88</sub> Fe <sub>2.12</sub> O <sub>4</sub>	8.343	0.11	0.255
Ni <sub>0.6</sub> Fe <sub>2.4</sub> O <sub>4</sub>	Ni: 12.34%; Fe: 60.14%	Ni <sub>0.58</sub> Fe <sub>2.42</sub> O <sub>4</sub>	8.362	0.1	0.212

<sup>7</sup> All samples were made by Remington Rand Univac, Division of Sperry Corporation.

<sup>8</sup> J. R. Clement and E. H. Quinell, Phys. Rev. **92**, 258 (1953).

specific heats for copper,<sup>9</sup> carbon,<sup>10</sup> Bakelite,<sup>11</sup> and Glyptal<sup>12</sup> (this quantity was, for every temperature less than 0.1 times the heat capacity of the ferrite), we obtained the heat capacity of the ferrite.

The calorimeter, shown in Figs. 3(a) and 3(b), employed a heat switch rather than an exchange gas, so that no helium gas came in contact with the sample prior to specific heat measurements, thereby avoiding helium desorption effects. The calorimeter was flushed with nitrogen gas prior to each measurement and then evacuated to  $1\text{-}\mu$  pressure. The all-metal needle valve was then closed with the sample in the position shown in Fig. 3(b). The system was cooled to liquid helium temperature, after which liquid helium was admitted into the Dewar. In this way the sample could be quickly cooled to  $77^\circ\text{K}$ , after which the nitrogen gas condensed, leaving a vacuum which was probably better than could have been obtained with a diffusion pump. The heat switch was then operated by engaging the raising and lowering catch and turning the screw mechanism of the Veeco bellows valve. The sample was then forced against the bottom of the calorimeter and cooled to the temperature of the helium bath. A sample could be cooled from  $77^\circ\text{K}$  to  $4.2^\circ\text{K}$  in approximately 11 min with this switch. At  $1.2^\circ\text{K}$  the release of the switch heated the sample from  $1.2^\circ\text{K}$  to  $1.6^\circ\text{K}$ , thereby limiting our lowest temperatures.

With the sample in a raised position at  $1.6^\circ\text{K}$  the heating cycles (5 min on, 5 min off) were started and continued consecutively until  $5^\circ\text{K}$  was reached. Neither the indium O-ring which sealed the bellows movement to the top of the calorimeter nor the bellows movement showed any superfluid leaks after 23 cyclings between room temperature and  $4.2^\circ\text{K}$ . In this way one measurement of heat capacity was obtained every ten minutes.

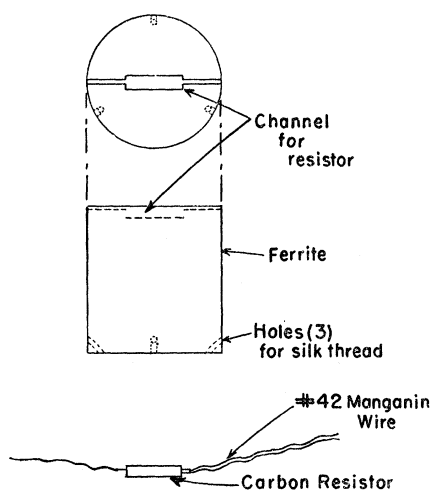


FIG. 2. Preparation of the sample for the calorimeter.

<sup>9</sup> W. H. Keesom and J. A. Kok, *Physica* **3**, 1035 (1936).  
<sup>10</sup> P. H. Keesom and N. Pearlman, *Phys. Rev.* **99**, 1119 (1955).  
<sup>11</sup> Extrapolated from data of Hill and Smith [R. W. Hill and P. L. Smith, *Phil. Mag.* **44**, 636 (1953)].  
<sup>12</sup> N. Pearlman and P. H. Keesom, *Phys. Rev.* **88**, 398 (1952).

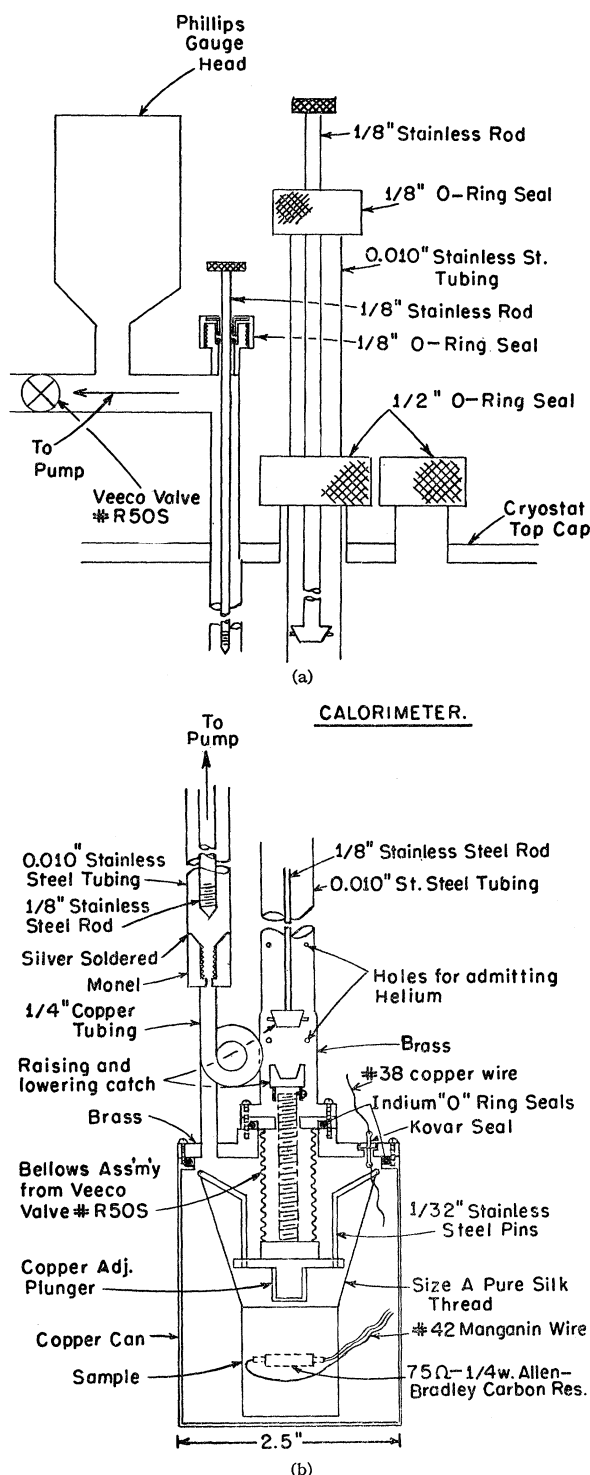


FIG. 3. Calorimeter: (a) top section; (b) calorimeter can.

## V. DISCUSSION OF DATA

Four separate sets of measurements were made on  $\text{Ni}_{0.94}\text{Fe}_{2.06}\text{O}_4$  with different power inputs, for varying lengths of time and with different heaters, and there were no consistent differences in the results obtained.

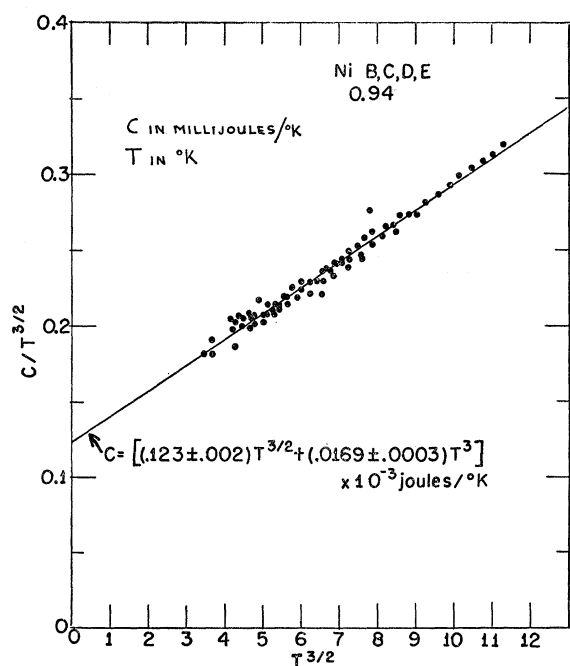
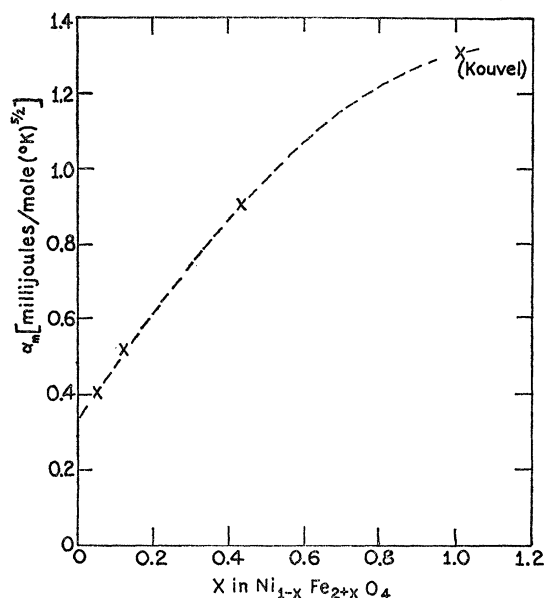
TABLE III. Specific heat results.

Material	$\alpha_M$ [millijoules/ mole ( $^{\circ}\text{K}$ ) $^{3/2}$ ]	$\sigma_{\alpha}$ Standard deviation	$\beta$ [millijoules/ mole ( $^{\circ}\text{K}$ ) $^4$ ]	$\sigma_{\beta}$ Standard deviation	$A$ ( $10^{-7}$ erg/cm) Landau-Lifshitz exchange constant	$\Theta_D$ Debye temp. ( $^{\circ}\text{K}$ )
$\text{Ni}_{0.94}\text{Fe}_{2.06}\text{O}_4$	0.407	$\pm 0.007$	0.0557	$\pm 0.0011$	3.03	$625 \pm 7$
$\text{Ni}_{0.88}\text{Fe}_{2.12}\text{O}_4$	0.513	$\pm 0.008$	0.0452	$\pm 0.0011$	2.83	$670 \pm 8$
$\text{Ni}_{0.88}\text{Fe}_{2.42}\text{O}_4$	0.899	$\pm 0.018$	0.0607	$\pm 0.0025$	2.02	$608 \pm 10$
$\text{Mg}_{0.83}\text{Fe}_{2.18}\text{O}_4$	0.369	$\pm 0.010$	0.0306	$\pm 0.0012$	1.64	$762 \pm 15$
$\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$	0.680	$\pm 0.018$	0.1015	$\pm 0.0024$	2.27	$512 \pm 5$
$\text{Co}_{0.33}\text{Fe}_{2.17}\text{O}_4$	0.563	$\pm 0.026$	0.0687	$\pm 0.0035$	3.12	$584 \pm 10$
$\text{Fe}_3\text{O}_4$ (Kouvel)	1.315		0.047		1.8	660

Figure 4 shows the results of these four separate experiments, shown using the same symbols for clarity, performed on  $\text{Ni}_{0.96}\text{Fe}_{2.04}\text{O}_4$ . The data are plotted as  $C/T^{3/2}$  vs  $T^{3/2}$ , so that from Eq. (8) the  $T^{3/2}=0$  intercept is  $\alpha_M$  and the slope is  $\beta$ . The straight line is the line obtained by at least-squares fit to the data and the given errors in  $\alpha_M$  and  $\beta$  are the standard deviations obtained by the least-squares analysis. The standard deviations agreed with calculated experimental errors, which were principally due to the error in measuring the heat leak, and were, for all samples, within  $\pm 3\%$ . The data taken on all the samples were plotted in this way and the values of  $\alpha_M$  and  $\beta$ , normalized to one mole of sample, are shown in Table III. The values of the Landau-Lifshitz exchange constant  $A$  and the Debye temperature  $\Theta$ , calculated from these values of  $\alpha_M$  and  $\beta$  using Eqs. (7) and (9), respectively, are also shown in Table III. The Debye temperatures are in good agreement with the values obtained by liquid

nitrogen specific-heat measurements.<sup>13,14</sup> The values of  $A$ , however, are all smaller (by a factor of approximately 3) than anticipated from measurements of the Curie temperature. The value of  $\alpha_M$  for magnetite, as obtained by Kouvel (see Table III) is also too large, thereby causing  $A$  to be too small.

There are several possible reasons for the discrepancies between the parameters measured in this experiment and the values of these parameters inferred from observed Curie temperatures. One is the failure of the Weiss field theory to adequately describe the relationship between the Curie temperature and the exchange integral. This failure has motivated others<sup>15-18</sup> to seek a more accurate expression for ferromagnets, and an extension of their work to include ferrimagnets may provide the solution of this problem.

FIG. 4.  $C/T^{3/2}$  versus  $T^{3/2}$  for nickel ferrite.FIG. 5.  $\alpha_M$  versus  $x$  in  $\text{Ni}_{1-x}\text{Fe}_{2+x}\text{O}_4$ .

- <sup>13</sup> E. G. King, J. Phys. Chem. **60**, 410 (1956).
- <sup>14</sup> R. W. Millar, J. Am. Chem. Soc. **51**, 215 (1929).
- <sup>15</sup> W. Opechowski, Physica **4**, 181 (1937); **6**, 1112 (1939).
- <sup>16</sup> V. Zehler, Z. Naturforsch. **5A**, 344 (1950).
- <sup>17</sup> P. R. Weiss, Phys. Rev. **74**, 1493 (1948).
- <sup>18</sup> H. Callen and G. Horwitz (to be published).

Another possible explanation may lie in the purity of the samples. Early measurements<sup>19,20</sup> of the specific heat of yttrium iron garnet also yielded large values for  $\alpha_M$ . These were later found<sup>6</sup> to be due to orthoferrite impurities and magnetic rare-earth impurities on the weakly exchange-coupled rare-earth sublattice. The samples measured here, however, were all x-rayed and there were no perceptible traces of orthoferrite structures on the Debye-Scherer x-ray pattern in any sample. Figure 5 shows a plot of  $\alpha_M$  vs  $x$  for the iron-nickel ferrite system  $\text{Ni}_{1-x}\text{Fe}_{2+x}\text{O}_4$  and includes the results of three samples measured here and Kouvel's sample at  $x=1$ . As  $x$  is increased from zero to one,  $\alpha_M$  increases, approaching the value obtained by Kouvel. Recalling that the three nickel samples were polycrystals, sintered from commercial chemicals while the  $\text{Fe}_3\text{O}_4$  sample was a natural single crystal, and recalling that all the values of  $\alpha_M$  yielded Curie temperatures that were approximately the same factor too small (see Table IV), it would seem unlikely that the quantity of an impurity causing the large values of  $\alpha_M$  would have varied in such a regular fashion.

TABLE IV. Curie temperatures.

Material	$T_c$ (calculated) (°K)	$T_c$ (observed) (°K)
$\text{Ni}_{0.96}\text{Fe}_{2.04}\text{O}_4$	284	850
$\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$	201	940
$\text{Co}_{0.83}\text{Fe}_{2.17}\text{O}_4$	362	790
$\text{Fe}_3\text{O}_4$ (Kouvel)	238	848

It also seems unlikely that  $A$ - $A$  and  $B$ - $B$  exchange interactions could have caused the large values of  $\alpha_M$  since Kouvel<sup>1,2</sup> has shown that  $\alpha_M$  is not seriously affected by reasonable values of  $J_{AA}$  and  $J_{BB}$ .

The observed heat capacity of cobalt ferrite was somewhat different than the other ferrites measured. Its heat capacity increased at lower temperatures as can be seen in Fig. 6. This was attributed<sup>21</sup> to the nuclear heat capacity which arises from the interaction between the nuclear magnetic moment of  $\text{Co}^{59}$  and the hyperfine field at the nucleus due to orbital electrons. Bleaney<sup>22</sup> and Marshall<sup>23</sup> have shown that this nuclear heat capacity should be proportional to the reciprocal temperature squared. The quantity  $\gamma T^{-2}$  was therefore subtracted from the observed heat capacity as is also shown in Fig. 6. The value of  $\gamma$  was chosen so as to minimize the standard deviation in the least-squares plot of  $(C_v - \gamma T^{-2})/T^{3/2}$  versus  $T^{3/2}$ . This curve along with  $C_v/T^{3/2}$  versus  $T^{3/2}$  is shown in Fig. 7. The value of  $\gamma$

<sup>19</sup> D. T. Edmonds and R. G. Petersen, Phys. Rev. **102**, 1230 (1956).

<sup>20</sup> H. Meyer and A. B. Harris, Suppl. J. Appl. Phys. **31**, 495 (1960).

<sup>21</sup> Suggested by D. Baldock (private communication).

<sup>22</sup> B. Bleaney, Phys. Rev. **78**, 214 (1950).

<sup>23</sup> W. Marshall, Phys. Rev. **110**, 1280 (1958).

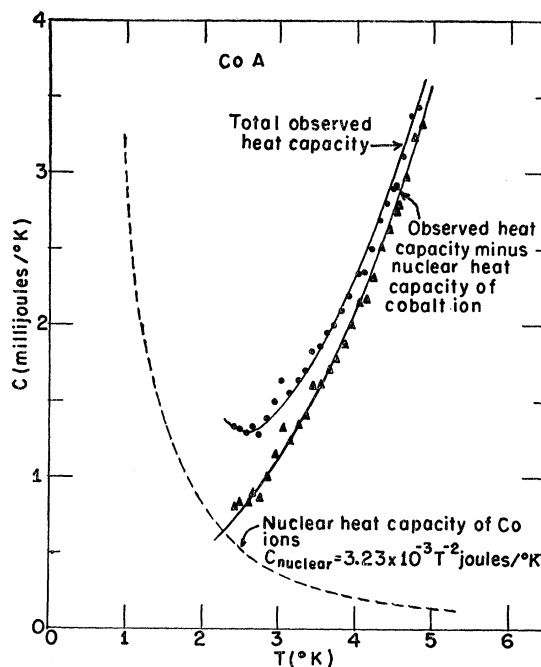


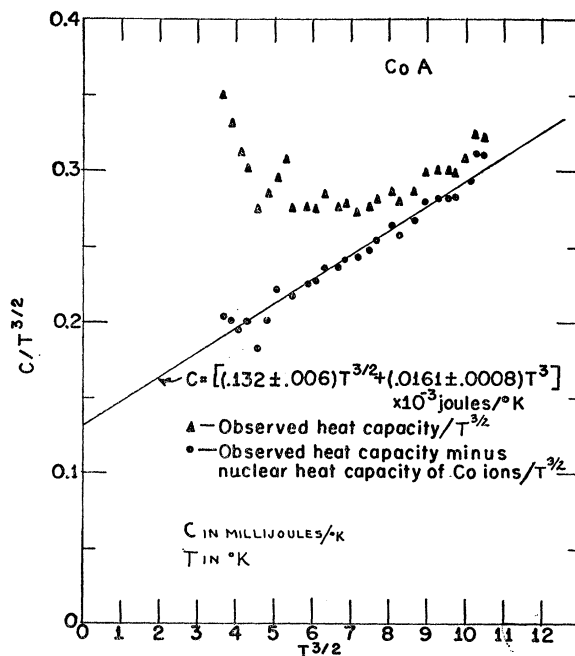
FIG. 6. Heat capacity of cobalt ferrite versus temperature for a 0.235 mole sample.

obtained in this way is

$$\gamma = 3.23 \times 10^{-3} \text{ joules} \cdot \text{°K}.$$

Normalizing  $\gamma$  to one mole of cobalt yields

$$CT^2/R = (20 \times 10^{-4}) (\text{°K})^2, \quad (13)$$


 FIG. 7.  $C/T^{3/2}$  versus  $T^{3/2}$  for a 0.235 mole sample of cobalt ferrite.

where  $C$  is the nuclear molar specific heat of the cobalt ions, and  $R$  is the universal gas constant. Using the expression for  $CT^2/R$  derived by Marshall<sup>23</sup> for ferromagnetic media, namely,

$$CT^2/R = \frac{1}{3}I(I+1)(g_N\mu_N H_N/k)^2,$$

where  $I$  is the nuclear spin (for  $\text{Co}^{59}$ ,  $I = \frac{7}{2}$ ),  $g_N$  is the nuclear  $g$  factor,  $\mu_N$  is the nuclear Bohr magneton, and  $H_N$  is the magnetic field at the nucleus, we computed  $H_N$  and obtained the value,

$$|H_N| = 410 \times 10^3 \text{ oe} \pm 10 \times 10^3 \text{ oe}. \quad (14)$$

This field is in excellent agreement with the theoretical calculations of  $H_N$  for a doubly ionized cobalt atom by Freeman and Watson.<sup>24</sup> They obtain the value

$$|H_N| \cong 435 \times 10^3 \text{ oe}. \quad (15)$$

The specific heat of manganese ferrite should also contain a nuclear contribution since it too has a large nuclear magnetic moment. However, nuclear specific heat data on manganese ferrite will not be as easy to interpret, since the manganese ions enter the crystal on both  $A$  and  $B$  sites with various valencies whereas cobalt enters the crystal on the  $B$  sites as a  $2+$  ion.

<sup>24</sup> A. J. Freeman and R. E. Watson, *Phys. Rev.* **123**, 2027 (1961).

Since ferrites have such small specific heats at low temperatures due to their large Debye temperatures and the absence of an electronic specific heat, this nuclear contribution should easily be distinguishable from the spin-wave and lattice specific heats without the necessity of going below  $1^\circ\text{K}$ .

We can conclude from these data that the  $T^{\frac{3}{2}}$  law for the magnetic contribution to the specific heat, as predicted by spin-wave theory, is valid. However, there is a serious discrepancy in the values of the exchange parameters when measured at low and high temperature.

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## Secondary Electron Emissions from Metal Surface by High-Energy Ion and Neutral Atom Bombardments

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To obtain  $\gamma_e$  for  $\text{H}_2^+$  ion bombardment on metal targets, an expression for the secondary electron emission coefficient by fast positive ion bombardment is obtained after adopting a method of calculation similar to that employed by Sternglass. It is shown that the experimental values of  $\gamma_e$  for  $\text{H}_2^+$  ion bombardment agree with the calculated values provided it is assumed that inside the target a hydrogen molecular ion is dissociated into a proton and a hydrogen atom, each having half the energy of the molecular ion. The dissociation cross section of a hydrogen molecular ion inside the target may be given by  $\sigma_d = K\sqrt{T}$ , where  $K = 1.2$ ,  $\sigma_d$  is expressed in units of  $10^{-17} \text{ cm}^2$ , and  $T$  is in Mev.

### I. INTRODUCTION

IT is well known that secondary electrons are emitted when metal surfaces are bombarded by positive ions. In the low-energy range (up to about 1 kev), the secondary electron emission coefficient  $\gamma_e$ , which is defined as the number of electrons emitted by the bombardment of one incident ion, varies directly with the ionization potential of the ion (potential ejection). Above 1 kev, the ejection depends primarily on the kinetic energy of the ion (kinetic ejection).

The secondary electron emission coefficient  $\gamma_e$  for high-energy hydrogen atom bombardment on a metal surface is also calculated and compared with experimental data. In the calculation, a neutral beam of hydrogen atoms is treated inside the target as composed of protons and electrons in addition to hydrogen atoms. Each of these three kinds of particles are capable of producing internal secondaries.

A fair agreement between the calculated and observed values of  $\gamma_e$  for  $\text{H}^+$ ,  $\text{D}^+$ ,  $\text{H}_2^+$ , and  $\text{H}^0$  bombardments has been obtained.

Secondary electron emission for potential ejection has been discussed theoretically by Oliphant and Moon,<sup>1</sup> Massey,<sup>2</sup> Shekhter,<sup>3</sup> Cobas and Lamb,<sup>4</sup> Varnerin,<sup>5</sup> and

<sup>1</sup> M. L. E. Oliphant and P. S. Moon, *Proc. Roy. Soc. (London)* **A127**, 388 (1930).

<sup>2</sup> H. S. W. Massey, *Proc. Cambridge Phil. Soc.* **26**, 386 (1930).

<sup>3</sup> S. S. Shekhter, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **7**, 750 (1937).

<sup>4</sup> A. Cobas and W. E. Lamb, Jr., *Phys. Rev.* **65**, 327 (1944).

<sup>5</sup> L. J. Varnerin, Jr., *Phys. Rev.* **91**, 859 (1953).