PHYSICAL REVIEW B VOLUME 18, NUMBER 7 1 OCTOBER 1978

Effects of finite size on critical phenomena: The resistivity anomaly in Ni films

H. Lutz,* P. Scoboria, J. E. Crow, and T. Mihalisin
Department of Physics, Temple University, Philadelphia, Pennsylvania 19122

(Received 16 December 1977)

The electrical resistivity of Ni films ranging in thickness from 250 to 24000 Å has been measured precisely near the Curie point. A shift in the temperature of the point where $d\rho/dT$ is maximum is observed which goes as $n^{-\lambda}$, where n is the number of atomic layers and the shift exponent λ is found to be 1.01 ± 0.10. The amplitude of the $d\rho/dT$ anomaly is observed to go as $\ln(n)$. Moreover, the shape of the anomaly is observed to broaden as one decreases n. Attempts to scale the data for all films along the lines suggested by Fisher and Barber are only partially successful and gave a rounding exponent θ of about 0.6. This value of θ is not considered to be reliable.

I. INTRODUCTION

In recent years there has been considerable interest in the behavior of systems undergoing critical-point phase transitions.[1-4] Theorists have been quite successful[5] in explaining the experimental results obtained for a wide range of systems such as ferromagnets, ferroelectrics, superfluids and liquid-gas systems. For the most part these experiments have been performed with three-dimensional bulk samples. Theory, however, deals with systems of various dimensions and it is found that the behavior of a system at a critical point is very dependent on the dimensionality of the system. This investigation was begun to study the fundamental differences in behavior that can arise in a sample of restricted dimensionality. In a thin-film sample one can expect that a crossover from three-dimensional-like behavior to two-dimensional behavior might take place when the temperature-dependent correlation length $\xi(T)$ is comparable to the thickness t. $\xi(T)$ is given by

$$\xi(T) = \xi_0 \epsilon^{-\nu} , \tag{1.1}$$

with ξ_0 typically of order 2 Å, the correlation exponent ν about $\frac{2}{3}$, and $\epsilon \equiv (T - T_c)/T_c$, one finds that for $\epsilon \sim 10^{-3}$ the correlation length is about 200 Å. Thus in the case of the ferromagnetic transition in Ni films one would expect the crossover region to occur about 0.6 K above the transition for a 200-Å-thick film. In fact, one would expect significant modifications of the behavior to occur well above this temperature since those portions of the film near the boundaries will be affected when $\xi(T)$ is considerably less than t.

Fisher and Barber[6] have predicted the effects of finite size on critical properties such as the specific heat and susceptibility. In particular, they predict a shift in the transition temperature T_c, and a reduction in the amplitude and a rounding of the anomaly. They in fact propose an extended scaling scheme wherein film-thickness invariant behavior can be obtained if both the property and the temperature are scaled by appropriate powers of the film thickness. Their predictions are qualitatively depicted in Fig. 1.

We have made precise measurements of the electrical resistivity ρ of Ni films ranging in thickness from 250 to 24 000 Å. Since $d\rho/dT$ has been shown[7,8] to be proportional to the specific heat in this system we have compared our results to the T_c shifts, amplitude, and broadening predictions of Fisher and Barber.[6] A brief review of current theories of size effects on critical behavior is presented in Sec. II. Previous experimental work is summarized in Sec. III. Section IV explains the reasons for choosing to study the electrical resistivity of nickel and outlines experimental procedures. Section V contains the results and analysis of the experiment.

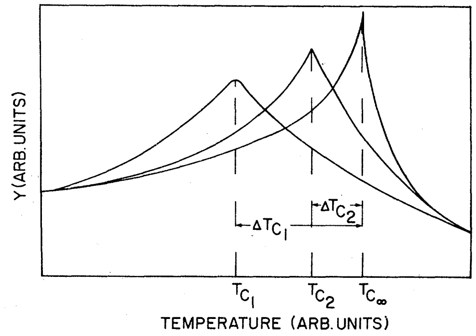

FIG. 1. Plot showing the predicted qualitative thickness dependence of some quantity Y that is divergent in a bulk system. Film 1 is thinner than film 2 and shows a greater depression in T_c and a broader and lower peak. The shift in T_c of the two thinner films is referenced against the transition temperature of an infinitely thick film.

II. THEORY OF FINITE - SIZE EFFECTS IN CRITICAL PHENOMENA

At present there is no theory which directly deals with the effects of finite size on the resistivity anomalies studies in this work. However, there does exist considerable theoretical[6, 9–12] work concerning the effects of finite size on thermodynamic quantities, such as the specific heat and susceptibility. Furthermore, as noted in the introduction, there exists a successful theory of resistivity anomalies in bulk ferromagnets proposed by Fisher and Langer,[7] which predicts that the quantity of interest in these studies $d\rho/dT$ should be proportional to the specific heat near T_c. Since it is quite likely that this theory remains valid for films (at least for those of sufficiently large thickness) it seems reasonable to use the theoretical predictions for the effects of finite size on the specific heat as a guide in the present studies on $d\rho/dT$. In this section, the results of current theory for the effects of finite size on thermodynamic quantities will be discussed. It is to be hoped that theorist will soon attack directly the effects of finite size on the transport anomalies such as $d\rho/dT$, so that direct comparison of the results of this study with a theory for $d\rho/dT$ can be made. In the absence of such a theory, however, the present thermodynamic predictions can serve as a guide.

The theoretical results summarized here[13] are applicable in general to "thick" films i.e., $t > 30\xi_0$. It should also be noted that the films in this experimental study fall into the thick range as for nickel, $\xi_0 \sim 2$ Å, and the thicknesses were in the range 250 Å $< t <$ 25 000 Å.

The simplest manifestation of a finite size effect is that the critical temperature is shifted when one makes one of the dimensions finite. Furthermore, the amount of this shift depends on the thickness t of the film. The shift in the critical temperature can be characterized by a critical exponent λ such that

$$[T_c(\infty) - T_c(t)]/T_c(\infty) \sim b/t^{\lambda} , \tag{2.1}$$

where $T_c(\infty)$ denotes the critical temperature of the bulk system, $T_c(t)$ that of the finite system, and b is a constant. If the finite system does not have a true critical point, as is often the case, one may still be able to talk about a "pseudocritical point" defined, for example, as the temperature where the specific heat is a maximum.

Another result of the theory is that the "crossover" temperature $\epsilon^*(t)$ at which the film switches from three- to two-dimensional behavior is characterized by a "crossover" exponent θ, such that

$$\epsilon^*(t) = [T^* - T_c(t)]/T_c(\infty) \sim C/t^{\theta} . \tag{2.2}$$

The definition of the crossover temperature $\epsilon^*(t)$ is not unique, as there is really a "crossover region" in which the system changes over from three- to two- dimensional behavior.

Fisher and Barber[6] introduced the theory of finite size scaling, in which they postulated that a property Y (such as the specific heat) obeys

$$Y(T, n) \sim n^{\omega} \chi(n^{\theta} \dot{\epsilon}) , \tag{2.3}$$

where $t = na$ (a is the atomic length of lattice spacing), $\theta = 1/\nu$, where ν is the three-dimensional correlation length exponent and $\dot{\epsilon} = [T - T_c(t)]/T_c(\infty)$. This is simply the statement that $\chi(T, n)$ is not a function of two independent variables T and n, but rather a function only of the combination $Z \equiv n^{\theta}\dot{\epsilon}$ (which is proportional to $(t/\xi)^{1/2}$ so that the only relevant scale is t/ξ).

Several predictions follow if the scaling ansatz is correct. In particular, for the special case where $Y \sim \ln(\dot{\epsilon})$ one must have

$$Y(T_c(n), n) = Y_{\max}(n) \sim \ln(n) . \tag{2.4}$$

Next, the relevancy of this theory to the present work should be noted. To begin with, the notions of a temperature shift and crossover behavior should hold equally well for transport anomalies, such as $d\rho/dT$, as for the thermodynamic properties discussed above. In addition, if the Fisher-Langer[7] theory remains valid for films, one would have

$$\frac{d\rho}{dT} \sim C \tag{2.5}$$

and in particular the finite size scaling theory for the specific heat would lead one to expect from Eq. (2.3) that

$$\frac{d\rho}{dt} = n^{\alpha_3/\nu} \chi(n^{1/\nu}\dot{\epsilon}) , \tag{2.6}$$

where α_d denotes the specific heat exponent of the d-dimensional system. Even if the Fisher-Langer[7] theory did not apply to nickel films, one might still expect $d\rho/dT$ to satisfy Eq. (2.3) but without requiring $\omega = \alpha_3/\nu$ as is predicted above.

The theory outlined above indicates three areas which might be investigated experimentally. The first area is the determination of the shift exponent λ. The second the value of the crossover exponent θ. And the third is to study the nature of the amplitude $A(n)$. There are at present several predictions as to what one might expect. There is the "naive" mean-field prediction proposed by Fisher and Ferdinand[14] in which $\lambda = 1$. There is also a "true" mean-field prediction of $\lambda = 2$ first proposed by Binder and Hohenberg[10] and subsequently rederived by Domb.[12] There is also a scaling theory of Fisher and Barber[6] and of Binder and Hohenberg[10] which predicts $\lambda = 1/\nu$. Finally Domb[12] has argued that in addition to the effect leading to $\lambda = 1/\nu$

there is also a competing effect which leads to $\lambda = 1 + \eta$, where η is the order-parameter correlation function exponent, which in the Heisenberg model is approximately $\eta = 0.04$.

The prediction on the behavior of the amplitude for the case where the property $Y(n)$ shows a logarithmic singularity, such as the case of the specific heat, is that one should see a $\ln(n)$ dependence. If one looks at $d\rho/dT$ for nickel [and assumes that $Y(n)$ for the two-dimensional film remains finite, as seems likely],[15] one would expect to see the amplitude go as $n^{\alpha/v} \simeq n^{1/7}$, which is quite difficult to distinguish from a $\ln(n)$ dependence.

In Sec. V we analyze our data for Ni films in terms of the theoretical results mentioned above. In particular, we analyze the thickness dependence of the shift in T_c and the amplitude of the anomaly as well as attempting to determine the crossover or rounding exponent θ.

III. EXPERIMENTAL BACKGROUND

A. General remarks

Although there have been some experimental studies[16-23] on the thickness dependence of the Curie temperature in nickel films, the data from these studies are not of high enough quality to be compared with the current theories. There are several experimental areas which need attention in order to improve the quality of the data. First, the films of past studies were, in general, too thin for one to observe crossover phenomena. The films ranged in thickness from less than 20 Å to about 2000 Å. In the lower part of this range the films are about 10 atomic layers in thickness; this can lead to complications due to quantum-mechanical size effects. It is also quite difficult to insure that the thinner films are smooth and of uniform thickness since the surface tension tends to make then "aggregate." A second problem in earlier work is the lack of attention given to uniform sample temperature and precision temperature measurement. Large temperature gradients across a sample smear out the transition and make the precise determination of T_c difficult. A third problem is that very little data were taken, especially close to the transition temperature. Related to this problem is the method by which T_c is chosen, which can lead to large uncertainties.

Theory suggests that for a film of about 100 atomic layers one must approach the critical point to within about one degree in order that the correlation length become about the same order of magnitude as the film thickness. Thicker films require an even closer approach to T_c for this to happen. While the effects of finite sample size should manifest themselves even when the correlation length is smaller than the film thickness (that is, when one is further from T_c than one degree from a 250-Å film) the data from previous work is much too crude to compare with current theories.

B. Magnetization studies

The earliest determinations[16,17] of the thickness dependence of the Curie temperature in nickel films were from studies on the saturation magnetization. These works covered a thickness range of from 20 Å to about 500 Å. They showd a dramatic lowering of the transition temperature for the very thin films, as much as 300 K for a 20-Å film. For thicker films, they found "little change" from the bulk value where "little change" was meant to be a shift of as much as 50 K. There are several problems with this early work. First, the films were grown in a relatively poor vacuum (10^{-5} Torr) and, therefore, probably contained a great deal of trapped gas. This can have the effect of increasing the lattice spacing and thereby weakening the effective magnetic interaction thus leading to an exaggerated depression in T_c. A second problem was that the applied magnetic field was rather low (< 400 Oe), which was too weak to saturate the specimens. Later work[18] done in comparable vacuums but with higher fields (10 kOe) showed less lowering of T_c. Perhaps even more important is the fact that data from one study[17] was taken only in the temperature range of −100 °C to +200 °C. The magnetization versus temperature curves were extrapolated to find T_c. Using such a method to accurately determine T_c must be viewed with much skepticism. Later work[19] improved on these early studies by making films in an ultrahigh vacuum system and by applying fields of 10 kOe. These films apparently contained much less trapped gas and showed less lowering of the transition temperature. These films were also quite thin, ranging from 3 to 200 Å. Moreover, data was taken only at 77 and 300 K and the transition temperature was inferred from this data so that precise location of T_c is questionable. Figure 2 shows the thickness dependence of the shift in T_c found by several authors.

C. Resistivity and other transport measurements

Magnetization studies of thin films prove to be difficult to perform. Other experimenters[20-23] tried using the anomaly in the resistivity to locate T_c. Early work[20] was on very thin films (<100 Å). This study showed a large depression of T_c with decreasing thickness; however, no information about pressure during evaporation or rate of

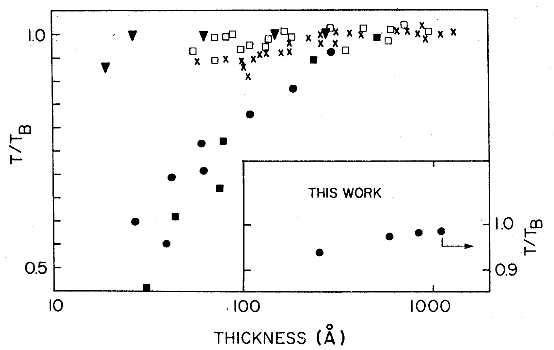

FIG. 2. Plot of the transition temperature T divided by the bulk transition temperature T_B versus film thickness in Angstrom units for various authors (Ref. 25). ● Drigo; ■ Crittenden and Hoffman; ▼ Neugebauer; □ Morita and Taniyama (technical vacuum); × Morita and Taniyama (ultrahigh vacuum). The inset shows the results of this work in this thickness range.

evaporation was given. Only about eight data points were taken over the temperature range of 300 to 400 °C and their ability to accurately determine T_c is in doubt.

Later work was presented in series of three papers[21-23] which considered the effects of impurities entering the films in various ways. These studies were done primarily on films from about 50 to 1000 Å and showed considerable scatter however, they do point out many problems to be avoided if one wishes to make high quality nickel films.

The first paper[21] attempted to determine the effect of impurities by varying the ratio of the residual pressure to the rate of evaporation from 10^{-7} to 10^{-5} Torr Å^{-1} sec. The films were coated with magnesium fluoride after evaporation to avoid oxidation. It was found that films that were made with a larger vacuum to evaporate rate ratio had lower transition temperatures indicating the importance of residual gas in the films.

The second paper[22] in the series considered the effect of outgassing the substrates for different lengths of time before evaporation and the effect of exposing the film to air after evaporation. It was thought that gas molecules adhering to the surface of the substrate would be trapped by the evaporated film and diffuse into the film as it annealed. Gas molecules could also adhere to the film after it had been made and then diffuse into it. The ratio of pressure to evaporation rate in this study was 10^{-7} Torr Å^{-1} sec. Although the data showed much scatter, it was clear that residual gas could enter the film from the substrate surface or from exposure to air and thus lower T_c. X-ray studies of the films showed that the thinnest films had an increase in their lattice spacing while the films thicker than 200 Å showed bulk lattice spacing.

The third paper[23] in the series used an ultrahigh vacuum system obtaining a vacuum-to-rate of about 10^{-9} Torr Å^{-1} sec. The substrates were outgassed for about one day at 400 °C before evaporation took place. The films were not exposed to atmosphere after fabrication. The transition temperature was determined from electrical resistance, magnetoresistance, and Hall-effect curves. Data was taken about 10 °C apart in the range 300–400 °C. Again T_c was found by locating the sharp break in the appropriate curve. The results were much like before, little depression in T_c for the thicker films but with too much scatter to compare with current theories. Figure 2 shows the shift in T_c found in this final study.

While these studies show how to make a high quality nickel film, they do not address themselves to the problem of taking high-quality data close to the transition point. Taking data points 10 °C apart means that one can approach the transition point only to within an ϵ of about 10^{-2}. This makes the location of a break in a resistance versus temperature curve good to ± 10 °C at best. See Fig. 3, which shows data from the third paper. The location of the transition temperature is probably known with even less precision since T_c is the point of maximum slope in the resistance versus temperature curve. This point occurs at a lower temperature than the "break" in the curve. The effect being looked for should give shifts in

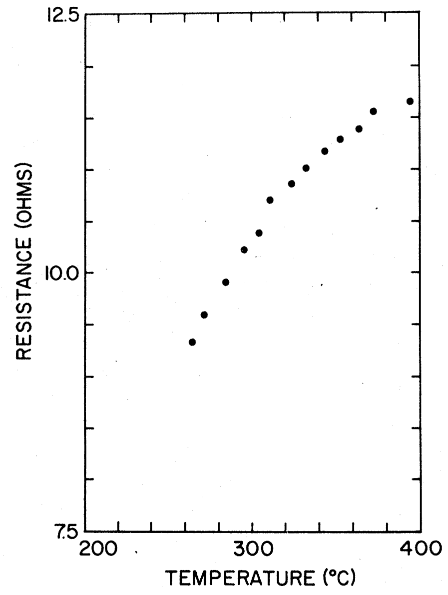

FIG. 3. Plot of resistance versus temperature from 200 to 400 °C for a nickel film of 320 Å (Morita and Tanayama).

T_c much smaller than 10 °C for thicker films, so a better method of finding T_c is required.

IV. EXPERIMENTAL PROCEDURES

A. Choice of system to study

In order to experimentally study the effects of finite samples size, one must be careful in the choice of an experimental system. The films must be of high quality, having well-defined bulk-like transitions in the extremely thick limit and be of uniform thickness. They must have few imperfections or impurities. They must remain stable during the course of the experiment. Since existing theories deal with films in the limit where the number of atomic layers becomes large, one must be able to grow thick films. The films must also have a transition temperature that is convenient to obtain experimentally and where good thermometry exists. Many systems were ruled out because they did not meet these criteria; among them were superfluid helium, rare-earth magnets, intermetallic compound magnets, and order-disorder materials. However, nickel meets all these criteria and is an ideal candidate for study.

B. Choice of property to investigate

The choice of a suitable property to measure is also an important consideration. Since current theories are written in terms of the thermodynamic quantities of specific and magnetic susceptibility, these two quantities seem to be promising candidates for study. However, they both have serious drawbacks. Thin-film specific-heat measurements suffer from the problem of substrate background, which severely reduces the sensitivity of the experiment. Magnetic-susceptibility measurements require relatively massive samples in order to give good sensitivity.

Several other properties demonstrate critical behavior. The Hall effect, for example, shows anomalous behavior at the Curie point but requires a temperature gradient ΔT to be applied across the sample. This severely limits how close one can approach T_c. The electrical resistivity does not require the application of a magnetic field or a temperature gradient and is not subject to background problems nor does it require massive samples. Resistivity measurements can easily be made to high precision (1 part in 10^5 is routinely done). Even though the resistivity is a transport property, it has been theoretically shown by Fisher and Langer[7] and experimentally demonstrated by Zumsteg and Parks[8] and that temperature derivative of the resistivity goes as the specific heat.

C. Experimental considerations in the measurement of the resistivity anomaly in nickel films

As mentioned earlier, the data previously taken on the resistivity anomaly in nickel films was insufficient in quantity and quality to make comparisons with current scaling theories. However, this early work did point out several pitfalls to be avoided in the current undertaking. Great care must be taken in preparing and running the films if one wishes to unambiguously ascribe the results to finite size effects rather than to impurities and imperfections in the films. Interstitial gas molecules must be kept from entering the films at all stages of the experiment. The substrate should be outgassed for about a day at high temperature to rid the surface of contaminates that could diffuse into the film. To minimize the number of gas molecules trapped during deposition, a low ratio of residual pressure to evaporate rate is desirable. The best previous work had this ratio equal to about 10^{-9} Torr $\mathrm{\AA}^{-1}$ sec. After deposition has been completed, the films are still susceptible to attack from residual gas in the system. At 1×10^{-7} Torr enough molecules strike the surface to form $\frac{1}{10}$ monolayer per second[24] (if the sticking coefficient is unity). Maintaining a low pressure helps, but for an experimental run that might take several days, sealing the films with some electrical insulator such as SiO is preferable. And, of course, the films should be made from the highest purity nickel available.

In addition to these precautions, there are several other areas which require attention in order to obtain high-quality data. First, to meet the "thick" film requirement of theory, thicker films than those used in earlier experiments should be grown. It has been suggested[25] that films thinner than 100 atomic layers (about 250 Å) not be used. The films should also be of uniform thickness so as not to get a distribution of transition temperatures. This can be achieved by first making the total area of the film small to minimize thickness variations due to nonuniform evaporation pattern from the evaporation source. Second, the substrate should be as smooth as possible to eliminate surface irregularities in the film.

Another area that needs careful attention is that of providing a uniform temperature environment for the samples. Any temperature gradient across the sample will smear out the transition. The best way to get a gradient-free environment at the transition temperature of nickel is to heat the sample radiatively in a thermally well-isolated cavity. Temperatures should be swept slowly both to avoid the formation of temperature gradients and to facilitate the taking of large quantities of data, especially close to T_c. Since in this experiment one does not know *a priori* where the critical point is, one must take closely spaced data over a wide temperature range. It is also important to have good data far above T_c in order to determine background terms and to make checks on film quality.

It is important, not only to minimize impurities and imperfections in the films, but also to try to insure that those residual impurities and imperfections that do exist are the same for all films. One way to do this is to make all the films at once under identical conditions and then run them all simultaneously.

The system described below was designed to fabricate eight films at once and then measure them *in-situ* while meeting the above criteria.

D. Vacuum system and electron-beam evaporation source

The vacuum system was a Varian Innovac with a 6-in. oil diffusion pump with water and liquid nitrogen traps modified to include a Meisner trap wound on the inside of the bell jar and a Varian Ti-ball titanium sublimation pump. This combination lowered the ultimate pressure of the system to 3×10^{-9} Torr.

The nickel was evaporated from an Airco Temescal model TIH-270 electron beam gun powered by a CV-10 10-kW power supply at rates of 100 Å sec. The nickel itself was Martz grade (99.995% pure) obtained from Materials Research Corporation. The overall vacuum to evaporation rate ratio was 10^{-9} Torr Å^{-1} sec, which was as good or better than the ratios obtained in previous work. Film thickness was monitored during evaporation by an Airco-Temescel DTC-10 quartz-crystal thickness monitor. A baffled resistance boat was provided to evaporate the SiO used to seal the films.

E. Furnace

The films were made and the resistivity measurements taken *in situ* without breaking vacuum. The furnace which provided a uniform temperature environment for the samples was suspended from the evaporator top plate by a piece of $\frac{1}{2}$in.$\times$0.010-in. stainless-steel tubing. Iron-constantan thermocouples and chromel-alumel thermocouples referenced to a large Dewar of distilled water and crushed ice made from distilled water were used for thermometry.

The furnace temperature was swept at a rate of about 3 K/hr. The furnace could reach temperatures in excess of 550 °C with gradients across the substrate of less than 10 mK.

F. Procedure

Nickel leads of approximately 1000 Å were evaporated onto the quartz substrate. The arrangement of the leads had circular symmetry to minimize the effects of any thermal gradients that may have been present. The leads were fashioned so that the same current would pass through each sample and two separate voltage leads would be present for each sample. The system was then opened up and the lead mask removed. Copper wires were attached to the nickel leads with Aremco-coat 543 high-temperature conducting copper print. An iron-constantan thermocouple was also cemented to the substrate using the copper print. A second stainless-steel mask for sample fabrication and subsequent SiO sealing was then attached to a rotary shaft. The system was then sealed and pumped down to a low pressure. The substrate was heated to a temperature of about 520 °C and allowed to outgas for several days. The temperature was then lowered to about 360 °C. The nickel was soaked in the electron beam gun until all signs of outgassing had ceased. The power to the electron gun was then increased until a rate of 100 Å/sec was achieved in a vacuum of 10^{-7} Torr. All eight samples were sequentially evaporated under the same vacuum and deposition rate conditions utilizing the rate monitor to determine the thickness of each and then sealed with SiO. The temperature was then raised again to 520 °C and the samples were allowed to anneal for several days until the resistivity was seen to drop by less than one part in 10^5 for a period of 8 h.

The resistance versus temperature run was then started. The temperature was swept downward at the rate of 3 K/h by slowly turning down the power going to the heaters. The taking of data was controlled by a Hewlett Packard 9820 programmable calculator. The thermocouple voltage was read to one part in 10^5, which allowed the temperature to be determined to 0.02 °C. Data were taken at 0.2 °C intervals. The current was read and voltage drop across the samples was read to one part in 10^5.

While thickness of the samples and the rate of deposition was monitored during evaporation by a thickness monitor, more accurate determinations of the thickness were made after the run had ended with a Sloan A-100 Angstrometer, which is a multiple beam interferometer. The thickness samples were first coated with a layer of aluminum to enhance the reflectivity of the surface. The accuracy was ± 25 Å for the films of thickness less than 1000 Å and better than 2% for the thicker films.

After the thickness was measured the residual resistivity ratio of each film was measured by comparing the room-temperature resisitivity to the resistivity at 4.2 K.

V. RESULTS AND CONCLUSIONS

A. Results

As mentioned earlier, an iron-constantan thermocouple was used for thermometry. Since thermocouple tables are only calibrated in 1° steps, the following method of interpolation is used. Smoothed thermocouple tables[26] for iron-constantan are divided into six temperature ranges. The temperature versus voltage data in each range are then fit to a polynomial of the form

$$T(V)=C_0+C_1V+C_2V^2+\cdots+C_nV^n \tag{5.1}$$

by a least-squares-fit technique. The order of the polynomial in each range is chosen so that the resulting function fits the table to better than 3 mK over the entire range. That range of temperatures into which the critical temperature of all the films fall is fitted by one polynomial to insure that no film will have its transition temperature near to where two temperature intevals meet. This prevents any mismatching where two polynomials join from introducing an erroneous temperature close to T_c.

The resistance versus temperature data was numerically differentiated using a sliding parabolic least-squares-fit technique. That is, a parabola is fitted to a group of adjacent points and the derivative of the parabola calculated at the middle point. This procedure is repeated at each experimental point. The number of points used in the fit can affect the shape of the derivative curve. By including more points in the fit, the effect of uncertainties in the R versus T curve are averaged out and the resulting dR/dT versus T curve is smoother. But including more points in the fit increases the temperature interval over which the derivative is being computed, and this can introduce numerical rounding into the dR/dT curve. The number of points used in the differentiation procedure for any given film was chosen so as to optimize the competing effects of smoothing and rounding.

Following the suggestion of Fisher and Barber,[6] the transition temperature of the films was chosen as the temperature at which the maximum in the temperature derivative of the resistivity occurs. Figure 4 shows a plot of $t\,(dR/dT)$ versus T and a plot of R/R_c (the resistance divided by the resistance at T_c) versus T for a film thickness 24140 Å. For clarity only every 20th data point is shown!

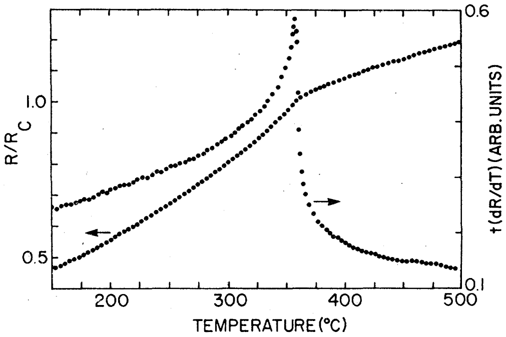

FIG. 4. Plot R/R_c vs T and tdR/dt vs T for film thickness 24 140 Å. For clarity only every 20th data point is shown.

Figure 5 shows plots of $t\,(dR/dT)$ versus T for three films of thickness 250 Å, 910 Å and 24140 Å. The quantity $t\,(dR/dT)$ is proportional to $d\rho/dT$ since all films have the same width and length. The similarity between this figure and Fig. 1 should be noted. Qualitatively, at least, the behavior is as expected.

B. Film quality

Before discussing quantitative results from this experiment, the quality of the films used should be discussed. If one wishes to ascribe the observed behavior to the effects of finite sample size rather than to film defects such as vacancies, strains, oxidation, etc., one must be confident about film quality. Although the methods used in preparing the films should guarantee that they be of sufficiently high quality, checks were made to insure that this was indeed so.

The phonon contribution to the resistance R_{phon} can be found by taking the difference between the room-temperature resistance and the resistance at 4.2 K, if one assumes that the magnetic contribution at 300 K may be ignored. A plot of R_{phon}

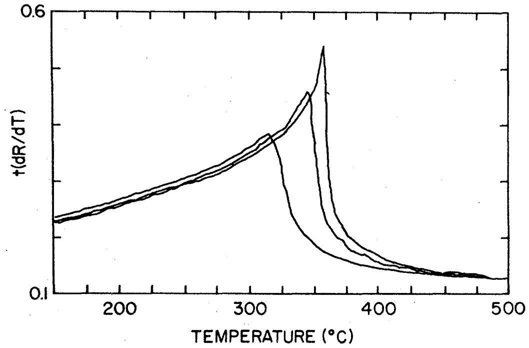

FIG. 5. Plot of tdR/dT vs T for three films of thickness 250 Å, 910 Å and 24, 140 Å. The points have been connected for clarity.

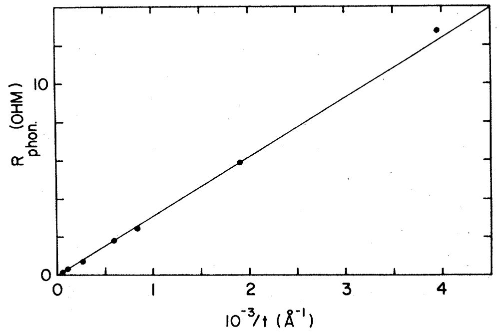

FIG. 6. Plot of phonon contribution to the resistance vs inverse thickness.

versus inverse thickness should give a straight line if the phonon resistivity is constant from film to film. Figure 6 shows that this is the case for these films.

The residual resistivity ratio (RRR) is defined as $R_{\text{phon}}/R_{4.2}$. A plot of $(\text{RRR})^{-1}$ versus inverse thickness should give a straight line if the impurity resistivity is constant from film to film and the boundary resistivity varies as t^{-1}. That is, one writes $R_{4.2}=(l/t\,\omega)(\rho_{\text{imp}}+a/t)$. Figure 7 shows that these films satisfy this requirement.

One can also look at $d\rho/dT$ at temperatures well above the transition temperature. This quantity should be constant if the phonon dominated lifetime and incoherent spin-flip scattering rate are not changing from film to film. Hence dR/dT should be proportional to t^{-1}. Figure 8 showing a plot of dR/dT at 520 °C versus t^{-1} is in agreement with this.

C. Comparison with theory

Next a quantitative comparison with theoretical predictions was performed. The data of shift in T_c versus film thickness were fit to the form

$$[T_c(\infty)-T_c(n)]/T_c(\infty)=bn^{-\lambda} \qquad (5.2)$$

using a least-squared routine with $T_c(\infty)$, b, and λ as free parameters. The resulting best-fit values are $T_c(\infty)=630.9\pm0.7$ K, $b=7.9\pm0.5$, and $\lambda=1.01\pm0.11$. Figure 9 shows a plot of $\ln\{[T_c(\infty)-T_c(n)]/T_c(\infty)\}$ versus $\ln(1/n)$ as well as the best-fit function to Eq. (5.2) above. Figure 10 shows a plot of σ^2 versus λ, obtained by fixing λ and allowing $T_c(\infty)$ and b to vary to minimize σ^2 for fixed λ.

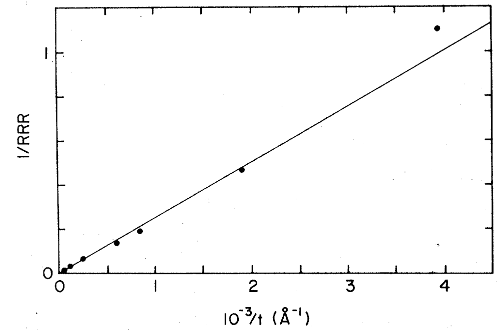

FIG. 7. Plot of the inverse residual resistivity ratio vs inverse thickness.

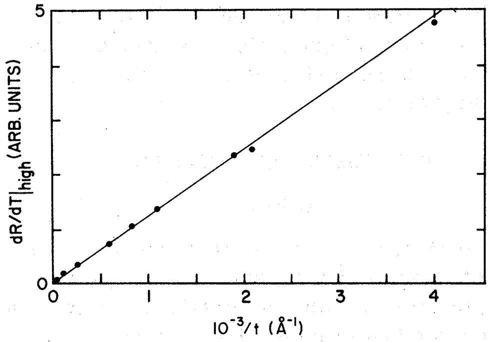

FIG. 8. Plot of dR/dT at 520 °C vs inverse thickness.

Here $T_c(\infty)$ is treated as a parameter because it is defined to be the transition temperature of an infinitely thick sample which has the same strains and other defects as the finite thickness films under investigation. In particular, $T_c(\infty)$ is not equal to the transition temperature T_B, of a well-annealed bulk nickel sample. Even if $T_c(\infty)$ were equal to T_B, using the value of T_B in fitting Eq. (5.2) would be questionable due to the inherent uncertainty in the absolute temperature indicated by a thermocouple, which is ±2 K in this range. When fitting data to Eq. (5.2), it is extremely important to realize that $T_c(\infty)$ and λ are highly correlated so that a least-squares fit must leave both parameters free if one is to obtain a reliable value for λ and the deviation in λ.

The value of $\lambda=1.01\pm0.11$ is not in agreement with the prediction of $\lambda=1/\nu$, advanced by Fisher

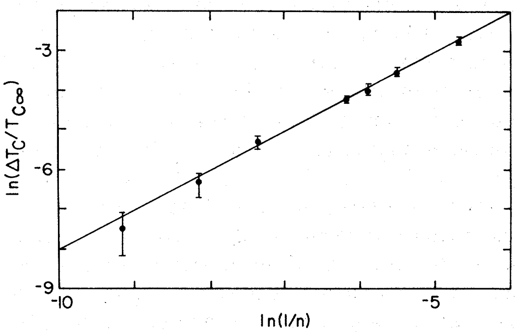

FIG. 9. Plot of $\ln[T_c(\infty)-T_c(n)]/T_c(\infty)$ vs $\ln(1/n)$. The line represents the best fit for the equation $\lambda=1.01\pm0.11$, $T_c(\infty)=630.9\pm0.7$ K, $b=7.9\pm0.5$.

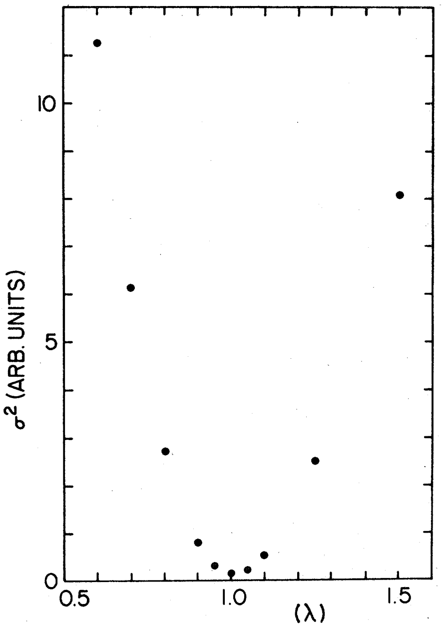

FIG. 10. Plot of σ^2 vs λ for Eq. (5.2). Here σ^2 is the sum of the squares of the deviations.

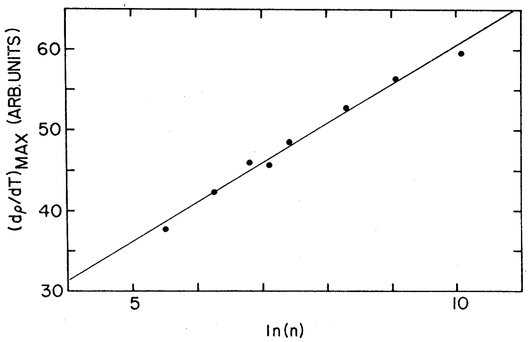

FIG. 11. Plot of $d\rho/dT|_{T_c}$ vs ln(n).

and Barber[6] and by Finder and Hohenberg,[10] which for nickel would give $\lambda \simeq 1.4$. There are two feasible explanations for this. First, there is the possibility that the experimental system has a constraint such as the "constant density" case mentioned in Ref. 6. If this were the case, a value of $\lambda = 1$ could possibly be expected. The experimental system does have one physical constraint. The system consists of a quartz substrate with a nickel film deposited on it. This is then covered with a coating of silicon monoxide. The nickel film, then, is "clamped" between the substrate and the SiO coating. The coefficient of thermal expansion for fused quartz in the temperature range of this experiment is approximately 5.5×10^{-7} K^{-1}; that of nickel is approximately 15×10^{-6} K^{-1}. Thus the nickel, which is deposited on the quartz, would like to expand or contract more than the substrate. This would have the effect of imposing a constant density constraint on the system. In addition, the coating of SiO can also constrain the system. When SiO is evaporated, it tends to get oxygen and, therefore, forms a film of SiO mixed with SiO_2 (Ref. 27). The exact mixture depends on the conditions during evaporation. The point is, however, that this coating would further constrain the nickel film. Thus the constraint of constant density could very well be realized in this experimental system. Whether or not this physical constraint could lead to a value of $\lambda = 1$ is not clear.

A second possible explanation is that the films made in this experiment might not be thick enough to meet the requirements of theory. The thickest film had only 10^4 atomic layers. It will be remembered that calculations[15] on Heisenberg lattice gave a lower value of λ than expected. One reason to doubt the results of these calculations is that the films considered were quite thin (the thickest had only six layers). Calculations[10] on other systems, however, indicate a value of $\lambda = 1/\nu$ for much thinner films than considered in this work. The thickness at which the scaling theories should hold in real films is still a matter of conjecture.

A second prediction of scaling theory is that concerning the thickness dependence of the amplitude of the anomaly. Figure 11 shows a plot of $d\rho/dT$ at the critical point versus ln(n). As can be seen, the results are consistent with a ln (n) dependence. A plot of $d\rho/dT$ at the critical point versus $n^{\alpha/\nu}$ with $\alpha/\nu \sim \frac{1}{7}$ also seems to be consistent with the data. As mentioned in Sec. II, it is quite difficult to distinguish between the two cases.

A third prediction of the theory is that $\theta = 1/\nu$. Thus θ can be determined if one realizes that Eq. (2.4) represents a "law of corresponding states." That is, if one were to make a plot of some quantity, such as $d\rho/dT$, normalized by n^{ω}, versus the scaled variable $n^{\theta}\dot{\epsilon}$ with the proper choice of θ, then one should find that all the points would line on a single curve. This procedure was attempted with the data. Figure 12 shows the normalized data $[\ln(n)]^{-1} d\rho/dT$ plotted as a function of $\dot{\epsilon}$. Note that this normalization is consistent with the findings of the thickness dependence of the amplitude of the anomaly. Figure 13 shows the "best attempt" to plot the data as a function of the scaled variable $n^{\theta}\dot{\epsilon}$. The value of θ obtained is $\theta = 0.6$. Here it was possible to obtain a value of θ that allowed the four thinnest films to scale reasonably well particularly for $T > T_c$. However, the thicker films did not scale with $\theta \sim 0.6$. Using $\theta < 0.6$ improved the results for the thick films but ruined the scaling for the thin ones. The value $\theta = 0.6$ differs markedly from theoretical predic-

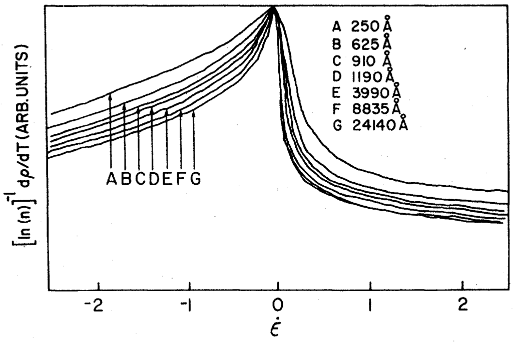

FIG. 12. Normalized $[\ln(n)]^{-1}d\rho/dT$ vs $\dot{\epsilon}$ for all films.

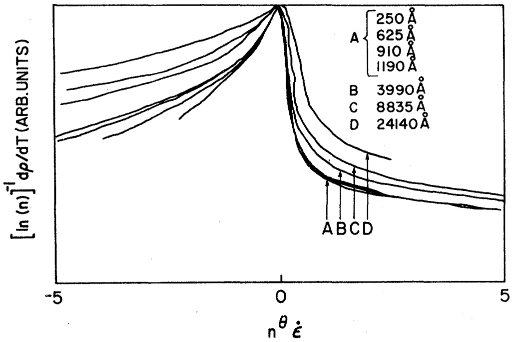

FIG. 13. $[\ln(n)]^{-1}d\rho/dT$ vs $n^{\theta}\dot{\epsilon}$ for all films with $\theta=0.6$.

tions. One crucial question to ask is whether or not one is close enough to $T_c(n)$ to see the effects of crossover. If one uses Fisher's criteria of $\xi\sim t$, then one would have $\epsilon^*=[T^*-T_c(n)]/T_c(\infty)\sim 1/n^{\theta}$. Table I shows tabulated values of ϵ^* for the expected value of $\theta=1/\nu=1.4$. Note that only the thinnest films have data inside this predicted crossover temperature. Of course, since the crossover temperature is so loosely defined, one might expect that crossover could manifest itself at a larger value of ϵ^*. For example, if one uses the criteria of crossover occurring when $\xi\sim 10^{-1}t$, then one sees that more films should be in the crossover regime (see Table I). Finally, if one were to accept the criteria of $\xi\sim t$ and assume that $\theta=0.6$ is correct, and this assumption on θ seems highly unlikely from a theoretical standpoint, then all the films should be in the crossover regime (see Table I). Ideally, of course, one would like to have data much closer to $T_c(n)$ than the crossover temperature so that one could observe two-dimensional behavior as well as crossover and three-dimensional behavior. It seems that this is not the case for this experiment. It is difficult to explain why the four thinnest films "seem" to scale while the others do not. If one was seeing scaling with $\theta=0.6$ then would expect that all films would scale. At this point, one should not have much confidence in the value obtained for θ.

One possible explanation of the thickness dependence of the $d\rho/dT$ anomalies must be considered in detail. One must explore the possibility that all of the effects, namely, the T_c shifts and the amplitudes and shapes of the transitions, are not due to finite size effects, but rather are due to a broadening of the transition caused by strains which may be correlated with the film thickness. This broadening of the transition would be due to a variation of T_c from grain to grain or perhaps within a given grain due to differing amounts of strain.

One model which has been used to consider such effects in bulk materials assumes that the T_c values obey a Gaussian distribution function characterized by a standard deviation of T_c values σ_{T_c}. Calculations using such a model show that for an asymmetric anomaly, such as the specific heat or $d\rho/dT$, the peak shifts to lower temperatures, the amplitude decays, and the breadth of the transition increases as σ_{T_c} increases. Since this behavior is qualitatively the same as the predicted finite size effects for decreasing film thickness, one must quantitatively evaluate the model to see if a correlation of thickness t and σ_{T_c} could account for the entire observed effects or at least suggest an explanation for the deviations from theoretical predictions, especially the lack of scaling for the thicker films and the anomalously low θ value obtained for the thinner films.

It should be noted that the observation that the

TABLE I. Values of ϵ^* for various choices of crossover criteria. The smallest value of $\dot{\epsilon}$ obtained for all films was $\sim 2.6\times 10^{-4}$.

t (Å)	ϵ^* ($\xi\sim t$, $\theta=1.4$)	ϵ^* ($\xi\sim 10^{-1}t$, $\theta=1.4$)	ϵ^* ($\xi\sim t$, $\theta=0.6$)
250	1.58×10^{-3}	3.96×10^{-2}	6.29×10^{-2}
625	4.37×10^{-3}	1.09×10^{-2}	3.63×10^{-2}
910	2.58×10^{-4}	6.49×10^{-3}	2.89×10^{-2}
1 191	1.77×10^{-4}	4.45×10^{-3}	2.46×10^{-2}
3 987	3.26×10^{-5}	8.20×10^{-4}	1.19×10^{-2}
8 835	1.07×10^{-5}	2.69×10^{-4}	7.41×10^{-3}
24 142	2.62×10^{-6}	6.59×10^{-5}	4.06×10^{-3}

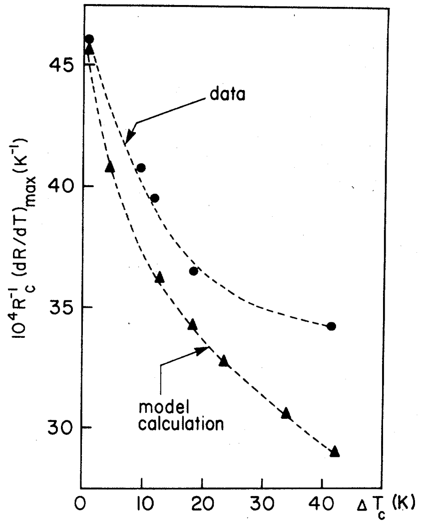

FIG. 14. $A(\Delta T_c)$ vs ΔT_c for both Gaussian rounding model and data.

residual resistivity $\rho_{4.2}$ is proportional to t^{-1} (consistent with boundary scattering) does not rule out a correlation of thickness t and σ_{T_c}. That is, the increase expected in $\rho_{4.2}$ for more highly strained films could also be proportional to t^{-1}.

In order to investigate whether or not Gaussian broadening might explain the data, one needs to compare the predictions of this model with experiment. At first sight there is some difficulty in making such a comparison since, for example, the model can give ΔT_c and the amplitude A as a function of σ_{T_c}, but of course, not as a function of the number of layers n (or equivalently the thickness t) while the data gives $\Delta T_c(n)$ and $A(n)$. This problem may be overcome by plotting $A(\Delta T_c)$ for both the model calculation and the data, hence eliminating the incompatible variables n and σ_{T_c}. Figure 14 shows the results for both the model calculation and the data. It should be stressed that the model calculation result has no adjustable parameters whatsoever. It uses the form $d\rho/dT = A\epsilon^{-\alpha} + B$ with parameters A, α, B, and T_c taken as those which fit the data of Ref. 8. From Fig. 14 one sees that for small ΔT_c (corresponding to thick films in the experiment and small σ_{T_c} in the model) the Gaussian rounding model could indeed explain the data fairly well. However, for larger ΔT_c (corresponding to thin films in the experiment and large σ_{T_c} in the model) very significant deviations between model and experiment occur. This result is indeed very encouraging in two respects. First, it supports our interpretation that the observed $A(n)$ and $\Delta T_c(n)$ behavior is due to finite size critical effects, not Gaussian rounding. Second, it suggests that the strong deviations from scaling observed for the thicker films is probably due to the strain broadening in these films being quite significant in comparison to the finite size effects for the closeness of approach T_c allowed by experiment. Moreover, it suggests that the anomalously small θ value which scales the thinner film results may be due to the fact that the Gaussian rounding even in these films is not entirely insignificant in comparison to the finite size effect. This interpretation is supported by the fact that an even smaller θ value would improve the scaling of the thicker films where the Gaussian rounding appears to be significant.

D. Conclusions

This work represents the highest precision study to date of the resistivity anomaly at the Curie point in nickel films. In addition, it is one of the first known attempts to verify the predictions of recent theories on finite size effects in critical phenomena. The value of $\lambda = 1.01 \pm 0.11$ is consistent with theoretical predictions if one adopts the possibility that the system is one with a constraint. It is also consistent with naive mean-field theory,[14] but this theory is generally considered to be invalid.[10,12] The result obtained should not be considered to support this theory. Domb has predicted that $\lambda = 1 + \eta$, which if one uses the best estimates of η for the Heisenberg model agrees with the value of λ found experimentally. However, the general theoretical pictures, both from exact and Monte Carlo calculations, seems to support[28] the $\lambda = 1/\nu$ hypothesis. Thus it seems likely at the moment that the results obtained for λ in this experiment can best be explained by the conjecture of Fisher and Barber that for a system with a "constant density" constraint one might expect $\lambda = 1$.

The data are also consistent with the prediction on the amplitude of the anomaly, although one can not distinguish between a $\ln(n)$ and $n^{\alpha/\nu}$ dependence.

The findings on the value of θ must at this point be considered very tentative. As discussed above the failure of the thicker films to scale and the scaling of the thinner ones with a θ value much smaller than $1/\nu$ may well be due to a small but not insignificant amount of rounding due to strains.

ACKNOWLEDGMENT

This work was supported by NSF Grant No. DMR-76-16433.

*Present address: Brookhaven National Laboratory, Upton, New York, 11973.

[1] M. E. Fisher, Rep. Prog. Phys. 30, 615 (1967).

[2] L. P. Kadanoff, W. Gotze, D. Hamblem, R. Hect, A. E. S. Lewis, V. V. Palciauskas, M. Royl, J. Swift, D. Aspnes, and V. Kane, Rev. Mod. Phys. 39, 395 (1967).

[3] P. Heller, Rep. Prog. Phys. 30, 731 (1967).

[4] H. E. Stanley, *Introduction to Phase Transition and Critical Phenomena* (Oxford University, New York 1971).

[5] K. G. Wilson and T. Kogut, Phys. Rep. 12C, 75 (1974).

[6] M. E. Fisher and M. N. Barber, Phys. Rev. Lett. 28, 1516 (1972).

[7] M. E. Fisher and J. S. Langer, Phys. Rev. Lett. 20, 665 (1968).

[8] F. C. Zumsteg and R. D. Parks, Phys. Rev. Lett. 24, 520 (1970).

[9] M. E. Fisher, in *Proceedings of the 1970 Enrico Fermi Summer School on Critical Phenomena, Verenna sul Lago di Como, Italy*, edited by M. S. Green, (Academic, New York, 1971),

[10] K. Binder and P. C. Hohenberg, Phys. Rev. B 6, 3461 (1972).

[11] M. E. Fisher, J. Vac. Sci. Technol. 10, 665 (1973).

[12] C. Domb, J. Phys. A 6, 1296 (1973).

[13] The notation and discussion here follow Ref. 6 closely.

[14] M. E. Fisher and A. E. Ferdinand, Phys. Rev. Lett. 19, 169 (1967).

[15] D. S. Ritchie and M. E. Fisher, Phys. Rev. B 7, 480 (1973).

[16] A. Drigo, Nuovo Cimento 8, 498 (1951).

[17] E. C. Crittenden and R. W. Hoffman, Rev. Mod. Phys. 25, 310 (1953).

[18] Y. Gondo, H. Konno, and Z. Funatogava, J. Phys. Soc. Jpn. 16, 2345 (1961).

[19] C. A. Neugenbauer, Phys. Rev. 116, 1441 (1959).

[20] K. Kuwahara, J. Phys. Soc. Jpn. 14, 1247 (1959).

[21] N. Morita, J. Phys. Soc. Jpn. 17, 1155 (1962).

[22] N. Morita and N. Inoue, J. Phys. Soc. Jpn. 20, 694 (1965).

[23] N. Morita and N. Taniyama, J. Phys. Soc. Jpn. 27, 1438 (1969).

[24] Airco Termescal, Vacuum Systems, Components and Technical Literature report no. 1 (1972/73), p. 218 (unpublished).

[25] M. E. Fisher (private communication).

[26] R. K. Adams and E. G. Davisson, Smoothed Thermocouple Tables of Extended Significance, ORNL-3649, Vol. 2 (1965) (unpublished).

[27] E. H. Blevis and R. D. Mathis, technical bulletin, R. D. Mathis Co. (unpublished).

[28] In an earlier experiment a value of λ consistent with $1/\nu$ was obtained. However, only one film was made per pump down and thus thermometry reproducibility was critical. As a result, the improved procedures reported here were instituted. Three separate experiments using these procedures have given $\lambda \sim 1.0 \pm 0.1$. As a result, the earlier agreement with $1/\nu$ must be considered fortuitous and the necessity of using the improved techniques reported here is clear. See Solid State Commun. 14, 1075 (1974).