Measurement of the Specific Heat of Nickel near Its Magnetic Critical Point*

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(Received 2 December 1968)

The specific heat of a nominally 99.999% pure nickel single crystal has been measured to within $\epsilon=10^{-5}$. The measurements are consistent with power-law descriptions over almost four decades in ϵ both above and below T_c. It is found that $\alpha'=-0.262\pm0.060$ and $\alpha=0.104\pm0.050$.

THIS paper reports measurements of the heat capacity of a nominally 99.999% pure single crystal of nickel to within 1 part in 10^5 of its Curie temperature $T_c=629.6$°K. Interest in critical-point phenomena has been stimulated in recent years by notable advances in both experimental and theoretical techniques.[1] The paramagnetic-ferromagnetic phase transition is a well-studied example of such a critical point, and the ferromagnet whose properties have been most thoroughly investigated is probably nickel.

It is usual to describe the asymptotic behavior of thermodynamic functions near a critical temperature by means of power laws. In particular, the behavior of the specific heat in zero applied magnetic field is assumed to be

$$\begin{aligned} C &\simeq A'\epsilon^{-\alpha'}+B', && \text{for } && T<T_c \\ &\simeq A'\ln\epsilon+B', && \text{for } \alpha'=0, && T<T_c \\ C &\simeq A\epsilon^{-\alpha}+B, && \text{for } && T>T_c \\ &\simeq A\ln\epsilon+B, && \text{for } \alpha=0, && T>T_c \end{aligned} \tag{1}$$

where $\epsilon=|(T_c-T)/T_c|$. Our data are consistent with these power-law descriptions over almost four decades in ϵ down to $\epsilon\simeq10^{-5}$.

These specific-heat measurements have been made using the traditional heat-pulse method, employing a vacuum adiabatic calorimeter designed to provide a high degree of temperature stability in the adiabatic shield and to minimize thermal gradients in the sample. The calorimeter consists of a water-cooled outer case, a proportionally controlled oven, a closely regulated adiabatic shield, and a sample holder containing the nickel crystal, heater, and thermometer. Miniature platinum-resistance thermometers were used for temperature measurement and control. The oven was regulated at a temperature about 15°C below that of the adiabatic shield. The adiabatic shield was controlled to within ±0.001°C. A 17-Hz bridge and phase-sensitive detector monitored the sample resistance thermometer with a resolution of ±0.0001°C. The uncertainty in relative temperature measurements was less than 0.002°C.

The 17-g sample was enclosed in a sample holder designed to keep any steady-state temperature gradients in the sample below 0.001°C. Measurement made with thermometers at each end of the sample holder showed that even during sample heating, gradients were less than 0.003°C.

Excellent isolation of the sample from the adiabatic shield kept sample temperature drift rates very small. During a typical 0.010°C change used for a specific-heat measurement, the drift rate would change less than 0.0004°C min^{-1}. Nevertheless, the adiabatic shield has a sufficiently short internal time constant (1 min) so that by lowering its temperature several degrees the sample could be rapidly cooled 0.010°C. The sample would return to near equilibrium at its base temperature in about 15 min. Repeated measurements taken at the same temperature were averaged to obtain a specific-heat point $C(T)$ with typical estimated standard deviations of 1.5% in C and 0.001°C in T.

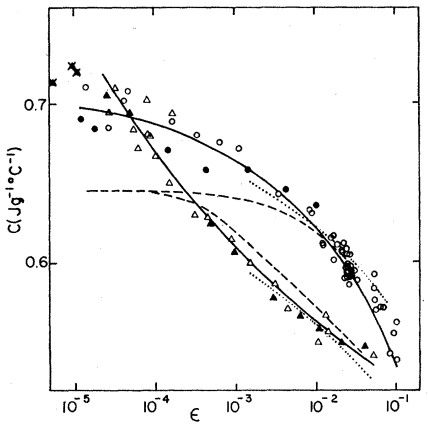

FIG. 1. Specific heat of nickel. Power laws fitted to the data from this experiment are shown as solid lines. Circles are data points for $T<T_c$; triangles are data points for $T>T_c$. Open circles and triangles belong to the first set of data; filled circles and triangles belong to the second set of data. The data of Handler *et al.* are shown as dashed lines. Weighted data from Ref. 2 are shown as dotted lines. The three points with superimposed ×'s are points above T_c which are too close to T_c and are not included in the power-law fits.

* Research supported in part by the National Science Foundation.

[1] M. E. Fisher, Rept. Progr. Phys. **30**, 615 (1967); P. Heller, *ibid.* **30**, 731 (1967).

The specific-heat points measured in this experiment are shown in Fig. 1 plotted against $\ln\epsilon$ using T_c chosen in the manner discussed below. Two sets of data points are shown. They have been normalized to a weighted average of previous data[2] for the range $|T-T_c|=3$–20°C. On our relative temperature scale, accurate to ±0.15°C, the critical temperature is

$$T_c=(356.485_{-0.009}^{+0.005})°\text{C}.$$

The uncertainty in T_c arises from the ambiguous predictions of the least-squares fitting procedure described below.

The data points in the first set were divided into three groups: the point with the maximum measured value of specific heat which was at T_m, the upper group of data points whose temperatures were above T_m, and the lower group of data points whose temperatures were below T_m. Power laws were fitted by least squares to both the upper and lower groups using α, α', and T_c as parameters, where T_c was restricted to the range between the maximum temperature in the lower group and the minimum temperature in the upper group. A minimum in the sum of the deviations squared gave the most probable values for α, α', and T_C. When the point at T_m was included in either the upper or lower group and the process repeated, the sum of the deviations squared clearly lacked a minimum in the new, smaller range of T_c. The apparent lack of rounding except at the point at T_m allowed the power-law fits over a 3.8 decade range in ϵ with a standard deviation of 1.3%. Even with the point at T_m excluded, such changes as elimination of most scattered points, weighting each point inversely proportional to its variance, or subtracting a Debye model lattice specific heat caused the predicted T_c to shift around in the region 356.476–356.480°C. As the position of the point at $T_m=356.4909$°C could also be a definition of T_c, $T_c=356.485$°C was selected as a compromise. The second set of data was treated in an identical manner. The relative temperature scale of the second set of data was transposed so that its T_c would agree with the T_c of the first set.

Values of α, α', and the other constants of the equations for the total nickel specific heat using data from both sets are:

$T>T_c$:

$$\alpha=0.104\pm0.050,\quad A=0.109,\quad B=0.389;$$

$T<T_c$:

$$\alpha'=-0.262\pm0.060,\quad A'=-0.2993,\quad B'=0.7138.$$

Much of each uncertainty arises from the uncertainty in T_c. Uncertainties of the critical indices are adequate to include all the variations in the fitting procedure mentioned above. The constants A and B are appropriate for the best-fit values of α and α' with unit weighting and no Debye model lattice specific-heat subtraction.

Previous measurements of the total specific heat of nickel[2,3] are also shown in Fig. 1. The older averaged data and the data of Handler *et al.* above $\epsilon=10^{-2}$ agree well with our measurements. Below this the Handler *et al.* results show a systematic rounding. Data from the present work show possible rounding only at the three points with the maximum measured values of specific heat which have $\epsilon<1.0\times10^{-5}$.

Griffiths has shown[4] that the general stability condition $C_M\geq0$ implies a thermodynamic inequality among the critical indices

$$\alpha'\geq2-\beta(1+\delta),\qquad(2)$$

where β and δ describe the critical behavior of the spontaneous magnetization and the magnetization along the critical isotherm: $M_s\sim\epsilon^{\beta}$, $|H|\sim|M|_{T=T_c}{}^{\delta}$. Our α' is negative: This changes the form of the Griffiths inequality. In Griffiths's proof his Eq. (7) reads

$$A(T_c,M_1)-A(T_c)\leq(T_c-T_1)[S(T_c)-S(T_1)],\qquad(3)$$

where A is the thermodynamic potential and S is the entropy. When α is negative, the right side will be proportional to $(B'/T_c)(T_c-T_1)^2$+higher terms, and the inequality becomes

$$(1+\delta)\beta\geq2.\qquad(4)$$

In fact, as Fisher has noted,[5] whenever the specific heat extrapolates to a finite value as T_c is approached from below, the inequality takes this form, i.e., that appropriate for $\alpha'=0$. Both recent sets of measurements of the magnetic properties of nickel in the critical region[6,7] are in accordance with the modified inequality.

It has been suggested by several authors[8–10] that the behavior of substances near their critical point might be described by a particular class of homogeneous equations of state. The experimental results noted above for the magnetic properties of nickel were analyzed using this approach.[6,7] In each case, a homogeneous equation of state was found to be a good fit to the data, but the functions found by the two groups are not the same. A consequence of the assumption of homogeneity is that certain scaling relations between the critical

[2] A standard set of values for $C(T)$ was obtained by weighting 2 for R. E. Pawel and E. E. Stansbury, J. Phys. Chem. Solids **26**, 607 (1965), 1 for C. Sykes and H. Wilkinson, Proc. Phys. Soc. (London) **50**, 834 (1938), and 1 for H. Moser, Z. Physik **37**, 737 (1936), where all T_c were superimposed and only $C(|T-T_c|)$ compared.

[3] P. Handler, D. E. Mapother, and M. Rayl, Phys. Rev. Letters **19**, 356 (1967).

[4] R. B. Griffiths, Phys. Rev. Letters **14**, 623 (1965).

[5] M. E. Fisher, J. Appl. Phys. **38**, 981 (1967).

[6] A. Arrott and J. E. Noakes, Phys. Rev. Letters **19**, 786 (1967).

[7] J. S. Kouvel and J. B. Comly, Phys. Rev. Letters **20**, 1237 (1968).

[8] B. Widom, J. Chem. Phys. **43**, 3898 (1965).

[9] C. Domb and D. L. Hunter, Proc. Phys. Soc. (London) **86**, 1147 (1965).

[10] A. Z. Patashinskii and B. L. Pokrovskii, Zh. Eksperim. i Teor. Fiz. **50**, 439 (1966) [English transl.: Soviet Phys.—JETP **23**, 292 (1966)].

indices should be obeyed.[11] Two of these are

$$\alpha=\alpha'=2-\beta(1+\delta). \quad (5)$$

Fisher[1] has shown that similar relations hold when the specific heat remains finite at T_c:

$$\alpha_s=\alpha_s'=2-\beta(1+\delta), \quad (6)$$

where the subscript s indicates that the coefficient is for the singular part of the specific heat, defined in Sec. 1.4 of Ref. 1. For a specific heat varying as Eq. (1) with $\alpha'\leq 0$, we find $\alpha_s'\leq-\alpha'$ and since the specific heat is already singular above T_c, $\alpha_s=\alpha$. Both sets of the scaling relations (5) and (6) seem to be violated. We therefore conclude that in the critical region the homogeneous function approach cannot be strictly correct.

[11] See, for example, R. B. Griffiths, Phys. Rev. **158**, 176 (1967).

It has been predicted[12] that the temperature derivative of the magnetic resistivity $d\rho_{\rm mag}/dT$ should be proportional to the magnetic specific heat. We did not subtract the poorly known C_p-C_v term from our data, but the values for α and α' that we find after first subtracting the lattice specific heat are almost identical to those quoted above. Craig *et al.* have measured $d\rho/dT$ for a nominally 99.999% pure sample of nickel,[13] and for $T>T_c$ their data show two regimes with different power laws and rounding and are not at all proportional to our specific-heat results. It does not seem, therefore, that the prediction[12] is correct, but it certainly would be desirable to make resistivity and specific-heat measurements on the same sample.

[12] M. E. Fisher and J. S. Langer, Phys. Rev. Letters **20**, 665 (1968).

[13] P. P. Craig, W. I. Goldburg, T. A. Kitchens, and J. I. Budnick, Phys. Rev. Letters **19**, 1334 (1967).

PHYSICAL REVIEW VOLUME 183, NUMBER 2 10 JULY 1969

Excitation of Electronic and Nuclear Spin Waves in a Flopped Antiferromagnet*

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Critical rf fields for parallel pumping in a flopped antiferromagnet are derived, and experimental results on excitation of electronic and nuclear spin waves in $RbMnF_3$ are reported. The theory includes expressions for the critical fields necessary for the excitation of two electronic spin waves, two nuclear spin waves, and one nuclear and one electronic spin wave. This involves computation of normal-mode frequencies and eigenvectors for the coupled nuclear and electronic spin systems. These normal modes for the flopped configuration show a high degree of ellipticity associated with the electronic motion, thus making the system ideal for spin-wave studies by parallel pumping. In particular, we predict that in the flopped state two nuclear spin waves can be excited in $RbMnF_3$ with critical rf fields of only about 0.1 Oe. Simultaneous excitation of one electronic and one nuclear spin wave by parallel pumping in $RbMnF_3$ has been performed in the temperature range from 2.4 to 13°K. Wave vectors up to 10^5 cm^{-1} are excited at a pumping frequency of 8.469 GHz. Using the experimental data to infer the product relaxation rates $\eta_k^e\eta_k^n$, we find order-of-magnitude agreement with Richards's theory for η_k^n and with Cole and Courtney's experimental value for η_k^e. In the product relaxation rates, there appears a minimum at a given k whose value increases linearly with temperature. There is no current theory which predicts such behavior. Excitation of two electronic spin waves could not be detected, since simultaneous electronic plus nuclear excitation was always the first process to become unstable.

I. INTRODUCTION

ELECTRONIC and nuclear spin waves have recently been excited[1,2] by parallel pumping techniques in $RbMnF_3$ and $CsMnF_3$ with external dc fields sufficiently large to reach the flopped-state configuration in these antiferromagnets. Feasibility of the experiments was predicted by the theory of Ninio and Keffer[3]; however, their calculations on ferrimagnets and antiferromagnets in low fields are not directly applicable to the flopped antiferromagnet. The purposes of this paper are to derive expressions for the critical rf fields for parallel pumping in flopped antiferromagnets and to present new data on our studies[1] of nuclear and electronic spin-wave excitation in $RbMnF_3$.

In addition to simultaneous excitation of nuclear and electronic spin waves and pure electronic spin-wave excitation, we also consider pumping of two nuclear spin waves and show that the threshold rf field for this process is likely to be lower than that for either of the two above-mentioned processes. An expression for threshold field h_c in simultaneous nuclear-electronic excitation was previously reported,[1] but it unfortunately

* Supported by U. S. Atomic Energy Commission. Helium gas supplied by a grant from the Office of Naval Research.

[1] L. W. Hinderks and P. M. Richards, J. Appl. Phys. **39**, 824 (1968).

[2] M. H. Seavey, J. Appl. Phys. **40**, 1597 (1969).

[3] F. Ninio and F. Keffer, Phys. Rev. **165**, 735 (1968).