Thermoelectric Power of Chromium below the Néel Temperature

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(Received 6 June 1972) The accurate determination of transport properties near the critical points is of great current interest.

We present here new data of 0.3% accuracy for the thermoelectric power S of chromium below the Néel temperature T_N which was obtained with a temperature difference of only 0.5 K. Extensive computer fitting to diverse theoretically predicted forms for S(T) does not yield an unambiguous critical exponent, nor does it let us make distinction between different forms. These ambiguities arise from our ignorance of the functional form of the normal background of S and the lack of precise knowledge of T_N . The latter is due to the fact that the transition is of first order, and, it can be argued, it masks a second-order transition occurring at a higher temperature if one approaches T_N from below. This higher temperature would then be the appropriate temperature for the analysis of fluctuation effects.

I. INTRODUCTION

In recent years the anomalous behavior of transport properties near critical points has received much of the attention that the divergences in the static properties did shortly before. There are three main reasons for this delay: First, the natures of the anomalies in electrical resistivity ρ , the thermal conductivity κ , and the thermopower S, for instance, are much less striking than those in the specific heat or the magnetization; second, the transport properties are experimentally more difficult to measure; third, theories predicting the anomalies were only recently developed. It can, of course, be argued that all these reasons depend on just one fact: The temperature derivatives of these transport properties, rather than the properties themselves, are divergent near the critical point.

Of the transport properties mentioned, only the electrical resistivity has been studied extensively.¹ This again is due to experimental difficulties in the measurement of thermal conductivity and thermopower as compared to the relative ease with which electrical resistivities can be measured. The problem, however, lies deeper: The imposition of a temperature gradient on the sample always limits the closest approach to T_C possible and with a gradient of ΔT it does not make sense to talk about an approach to T_C closer than $\frac{1}{2}\Delta T$. Thus, one would like to keep ΔT as small as possible. On the other hand, the quantity measured is generally proportional to ΔT and in order to measure it to a given accuracy one would like to have ΔT large. Since it is only the derivative of S that diverges at T_c , the gradient across the sample cannot be decreased as T_C is approached if it is to be measured with constant accuracy.

These are, however, not the only reasons why it is much harder to get, for example, thermopower data for chromium with an accuracy comparable to that of electrical-resistivity data for nickel. The ferromagnetic phase transition of Ni is well known to be of second order, while the nature of the antiferromagnetic transition in Cr is not-although it is hoped that it is of "nearly second" order with some of the effects of the fluctuations still noticeable. This means, among other things, that a firstorder transition interrupts what would have been a second-order transition at a higher (or lower) critical temperature, depending on whether one is approaching T_N from below (or from above), and, more importantly, that the second-order T_C cannot be measured, but only inferred from divergences. If this first-order transition is sufficiently far from the second-order transition it can happen that one has never even entered the critical region.

When measuring the resistivity of Ni, 2,3 one knows that the normal background contribution is quite linear and it can be subtracted. This is not the case for the thermopower of Cr; far below T_N the slope of S is of the same magnitude as and opposite sign from the slope at T_N . One last major difference concerns the forms of the functions predicted to fit resistivity and thermopower, respectively. Whereas it has been shown in a number of cases that

$$\frac{\partial \rho}{\partial T} \sim \frac{A}{\alpha} \quad (\epsilon^{-\alpha} - 1) + B \tag{1}$$

gives excellent fits over a large range of $\epsilon = |(T - T_C)/T_C|$, the proposed functions for the thermopower include forms with two different exponents of ϵ .

Available data on the thermopower anomaly near magnetic critical points are contradictory and confusing. Especially perplexing are the elusive oscillations in thermopower seen in some samples of Ni, ⁴ and in Fe and FeCr alloys⁵ near the Curie temperature.

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In this paper we present new data of 0.3% accuracy of the thermopower of chromium below the Néel temperature. We shall demonstrate that these data can be fitted equally well by a number of different expressions proposed in the literature. This leads us to the conclusion that data of much higher accuracy are needed to distinguish between different theoretical predictions.

II. THEORY

Two functional forms for the thermopower near the critical point of a magnetic system have recently been proposed. Tang, Craig, and Kitchens⁶ use the Gibbs-Duhem relation between the electrochemical potential and the entropy to show that for an itinerant-electron ferromagnet, like Ni, the excess specific heat at the Curie point can be related to the temperature derivative of the thermopower by

$$T\frac{\partial S}{\partial T} = c_{e1}^{\max}(eN_a n_e)^{-1} , \qquad (2)$$

where e is the charge of the electron, N_a is Avogadro's number, and n_e is the number of charge carriers per atom. This excess specific heat has been shown to be well described by a weakly divergent power law, ⁷ both above and below T_c

$$c_{\rm el}^{\rm mag} \sim \epsilon^{-\alpha} \,. \tag{3}$$

The temperature derivative of the electrical resistivity, in turn, has the same singularity as the specific heat⁸:

$$\frac{\partial \rho}{\partial T} \sim \epsilon^{-\alpha} \ . \tag{4}$$

Independent measurements of specific heat and resistivity² confirm Eqs. (3) and (4) with the same exponent α . In analogy to this, we propose to fit our data to an expression of the form⁹

$$T\frac{\partial S}{\partial T} = \frac{A}{\alpha}(\epsilon^{-\alpha} - 1) + \text{background.}$$
 (5)

We defer comments on the meaning of this relation and especially on the implied relation between specific heat and thermopower and, for the time being, simply accept Eq. (5) as one of the functional forms commonly used to fit critical data.

In the theory of Ausloos and Kawasaki^{10,11} the thermopower of Cr below the Néel point is given by

$$T\frac{\partial S}{\partial T} = \frac{B_1}{\alpha + \gamma - 1} \left(\epsilon^{-(\alpha + \gamma - 1)} - 1 \right) + \frac{B_2}{\frac{1}{2}(\alpha + \gamma)} \times \left(\epsilon^{-(\alpha + \gamma)/2} - 1 \right) + \text{background}, \quad (6)$$

where the first term is due to spin fluctuations and the second term to the appearance of energy gaps at the magnetic superzone boundaries. For S > 0 it should hold that $B_1 > 0$, $B_2 < 0$; the second term should dominate for small ϵ . As in Eq. (3), α is the exponent of divergence for the specific heat; γ is that of the staggered or sublattice susceptibility. The intimate theoretical connection between thermopower and resistivity is demonstrated again by the fact that Suezaki and Mori¹² have previously obtained an essentially identical expression for $d\rho/dT$.

We have written Eqs. (5) and (6) in the form that specifically allows for logarithmic singularities (when the exponent of ϵ goes to zero). Care must be taken that the determination of the coefficients A or B_i is not dominated by the term -1 in these expressions. This is done most easily by including a constant term, say, C, in the background.

For the real background function one is first tempted to consider the behavior of S for molybdenum and tungsten, ¹³ the two elements below Cr in the periodic table (Mo is the closer analog of the two since W is not strictly isoelectronic with Cr). One quickly sees that this is inappropriate since dS/dT for Cr well below T_N is considerably larger than that of either Mo or W. One must therefore look at the low-temperature data of Cr itself for a clue to the background. Data over a large temperature range^{14,15} indicate that the background is not a simple matter. There is no region where the thermopower is well approximated by a straight line. However, as we shall demonstrate, the introduction of a parabolic background cannot be justified either since any improvement in the fit is illusory, i.e., only due to the additional free parameter.

III. EXPERIMENTAL PROCEDURE

The sample was cut to the approximate dimensions $1 \times 0.1 \times 0.1$ cm with a low-speed low-pressure diamond cutting wheel (Macrotome) from a high-purity "Iochrome" crystal (Iochrome is the trademark of Materials Research Corporation). It was then given an acid etch in hydrochloric acid to remove the worked surface. Visual inspection revealed the sample to be composed of three large crystals; however, x-ray analysis showed that the orientation of these crystals is the same along the length of the sample. In any case, there is not expected to be anisotropy in electron transport properties in chromium since the electron propagation is always parallel to the magnetic lattice vector.¹ The residual resistance ratio $R_{300 \text{ K}} / R_{4.2 \text{ K}}$ of another crystal prepared by the same method was approximately 70. The electrode junctions were produced by spot welding copper leads to the sample.

The sample was mounted in a vacuum can immersed in a well-stirred 10-gal-water-antifreeze bath which was thermally insulated with two layers of Armaflex insulation and aluminum foil. For the initial cool-down liquid nitrogen was forced through a

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copper coil immersed in the liquid. A simple copper-bar cold finger connected to a reservoir of a mixture of dry ice and alcohol held the bath temperature constant below room temperature; above room temperature a proportional controller was used. The bath temperature was measured with a calibrated Leeds and Northrup platinum resistance thermometer. The temperature gradient across the sample was produced by a small Advance wire heater and measured by two glass-lead thermistors (Gulton Industries, Model 51CA3) mounted with Thermocoat HT (Omega Engineering) directly over the electrode junctions. The voltage drops across the two thermistors, which were in series and had room-temperature resistances of nominally 100 $k\Omega$ and a typical sensitivity of 5% K⁻¹, were measured by two type-K-5 Leeds and Northrup potentiometers. These were balanced simultaneously with a Hewlett-Packard 3420B potentiometer which monitored the current through the thermistors. This current was supplied by a 2-V lead storage battery and was typically 1 μ A. The thermal voltage across the sample was amplified by a factor of 10^5 with a Keithley 140 amplifier and read to $3\frac{1}{2}$ significant figures on a Fluke 8300 digital voltmeter.

Every few degrees during the run the Advance wire heater on the sample was switched off and the sample came to equilibrium at the bath temperature. This provided the calibration points for the thermistors against the platinum resistance thermometer. The power to the Advance wire heater on the sample was held constant during the whole run.

After several preliminary runs, it was determined that a temperature gradient of 0.5 K was the best compromise between producing a signal which could be resolved to the desired accuracy and obtaining closely spaced data points. Data were taken in the temperature interval 275-312 K. Equilibration time for each data point was typically 15 min after the bath had been raised to the new temperature.

IV. RESULTS

The first step in the data analysis was the calculation of the temperature differences along the sample. As described in Sec. II, the thermistors on the sample were calibrated against the platinum resistance thermometer measuring the bath temperature by switching off the heater establishing the gradient along the sample. The function

$$\ln R = (AT + B)/(T + C)$$

described the resistance-versus-temperature relation of the thermistors very well. *A*, *B*, and *C* were determined by least-squares analysis of 20 data points over a temperature interval 254 < T < 312K. The root-mean-square error for these fits was of the order of 1.5 mK. The temperature gradient, which was about 0.5 K, and the average temperature of the sample were thus determined to 1.5 mK.

The experimental thermopower of Cr vs Cu was then determined by dividing the measured voltage drop along the sample by the temperature difference. In order to arrive at the absolute thermopower of Cr we corrected from the measured values $S_{\rm Cr vs Cu}$ according to $S_{\rm Cr} = S_{\rm Cr vs Cu} + S_{\rm Cu}$, where¹⁶

$$S_{\rm Cu} = (-0.308 + 6.4 \times 10^{-3} T) \ \mu V \, {\rm K}^{-1}$$
 (7)

This step is not really crucial since the slope of S_{Cu} is much smaller than that of the normal background of Cr.

Figure 1 shows our experimental results for $S_{\rm Cr}$, as well as smoothed data of $\pm 1.2\%$ accuracy by Moore *et al.*¹⁴ which extend over a much wider temperature range. We also list our results in Table I. The combined uncertainties in the measurement of temperature difference (± 1.5 mK out of 0.55 K) and thermal emf ($\pm 0.01 \mu$ V out of 20 μ V) result in an over-all accuracy of about 0.3\%.

In order to compare the data to particular functional forms such as Eqs. (5) and (6), one would have to differentiate the data. However, due to the limited accuracy this procedure would introduce considerable scatter. One alternative to numerically differentiating the data would be a graphical differentiation, i.e., drawing a smoothed curve through the data points and taking the slopes of this curve with a protractor. This introduces a bias in the result which was deemed unacceptable. A second alternative—and the procedure followed in our analysis—is the integration of the functional forms.

Experimental runs over a wider temperature range indicate the presence of a distinct kink at 311 K, the thermopower being linear with tempera-



FIG. 1. Experimental thermoelectric power of chromium. Triangles: smoothed data by Moore *et al.* (Ref. 14), accuracy $\pm 1.2\%$. Circles: present work, accuracy $\pm 0.3\%$. The contribution of the Cu electrodes has been subtracted according to Eq. (7).

Temperature Thermopowe

(µV/K)

19.54

19.62

19.67

19.73

19.77

19.87

19.93

19.97

20.05

20.04 20.09

20.13

20.21

20.21

20.33

20.35

20.39

20.42

20.54

20.55

20.57

20.59

20.58

20.67

20.74

20.79

20.81

20.84

20.84

20.82

20.88

20.98

20.97

21.00

20.98

21.07

21.04

21.16

21,21

21.22

21.25

21.29

21.30

21.32

292,952

293.382

293.792

294.506

294.926

295,506

296.029

296.437

297.048

297.397

297.702

298.113

(K)

256.264

256.880

257.406

257.901

258.446

258.976

259.455

260.040

260.766

261,191

261.944262.457

263.049

263.474

263,969

264.442

264,998

265.587

266.245

266.658

267.019

267.372

267.748

268.144

268.518

268,905

269,332

269,623

270.007

270.392

270,274

271.124

271.779

272,338

272.689

273.145

273.602

274.133

274,623

275,154

275.834

276.312

276.857

277.349

bsolute thermoelectric power of chromium, S _{Cr} .				
r	Temperature (K)	Thermopower (µV/K)	Temperature (K)	Thermopower (µV/K)
	278, 193	21.48	298.485	21.53
	278.730	21.44	298.864	21.60
	279,177	21.52	299.230	21.62
	279.649	21.51	299.594	21.59
	280.184	21.54	299.969	21.57
	280,699	21.59	300.345	21.52
	281.337	21.61	300.649	21.50
	282.064	21,63	301,105	21.41
	282.534	21.70	301.516	21.43
	282.877	21.76	301,951	21.33
	283.374	21.71	302,389	21.36
	283.793	21.78	302,807	21.23
	284,240	21.81	303,149	21.22
	284.706	21.78	303.526	21.15
	285.282	21.81	303,886	21.12
	285.729	21.82	304,259	21.06
	285,992	21.82	304.652	21.01
	286,431	21.83	304.656	20.96
	286.940	21.82	305.051	20.93
	287.416	21.82	305.470	20.89
	288,884	21.90	305.877	20.85
	288.285	21.88	306.288	20.77
	288.693	21.86	306.682	20.70
	289,194	21.85	307.102	20.59
	289.489	21.88	307.523	20.52
	290.043	21.89	307.969	20.38
	290.492	21.81	308.393	20.29
	290.937	21.90	308.822	20.20
	291.375	21.83	309.255	20.10
	291.812	21.88	309.585	19.90
	292.238	21.86	309.820	19.80
	292.488	21.77	309,993	19.74

TABLE I. A

ture within experimental accuracy for 311 < T < 316K. At a slightly lower temperature, however, the absolute value of the first derivative starts increasing again; for our analysis we only consider data below 310 K, where the second derivative becomes positive.

We will thus write Eq. (5) as

$$T\frac{\partial S}{\partial T} = \frac{A}{\alpha} \left[\left(\frac{T_N - T}{T_N} \right)^{-\alpha} - 1 \right] + \text{background}$$
(8)

and integrate:

$$TS - \int_{T_0}^{T} S \, dT = \frac{-AT_N}{\alpha(1-\alpha)} \left(\frac{T_N - T}{T_N}\right)^{-\alpha+1} - \frac{A}{\alpha} T + \int_{0}^{T} (\text{background}) + F$$

310.220

310.437

310.658

310.876

311.329

311.533

311.807

311.998

312.241

312.409

312.647

19.64

19.53

19.40

19.31

19.03

18.96

18.86

18.83

18.75

18.71

18.69

Defining

21.66

21.64

21.72

27.66

21.67

21.66

21.68

21.63

21.64

21.62

21.60

21.60

$$Z=TS-\int_{T_0}^T S\,dT\,,$$

$$x=\frac{-T_N\epsilon^{1-\alpha}}{\alpha(1-\alpha)}-\frac{T}{\alpha},$$

we can write this as

$$Z = Ax + \int_0^1 (\text{background}) + F.$$

 T_0 is the temperature corresponding to the lowest experimental point and the constant F is $\int_0^{T_0} S dT$, which cannot be determined from our experimental data. For each exponent and Néel temperature chosen the quantity x can be calculated for each data point. A background contribution linear in the temperature, for example, leads to the form¹⁷

$$Z = Ax + BT^2 + CT + F$$

leaving four parameters to be determined.

For each choice of exponent and Néel temperature the root-mean-square (rms) deviation between measured data and calculated fit was determined. For this particular functional form the minimum rms value occurred for $\alpha = -0.3$ and $T_N = 310.15$ K. As an indication of the quality of the fit, we find that for this value of T_N the whole range of -0.7 $< \alpha < 0.0$ gives rms values within 10% of the minimum.¹⁸ If an rms value in this range is now used as a criterion we find that the following simpler forms are also valid:

$$T\frac{\partial S}{\partial T} = \frac{A}{\alpha} \epsilon^{-\alpha} + BT , \qquad (9)$$

$$T\frac{\partial S}{\partial T} = \frac{A}{\alpha}(\epsilon^{-\alpha} - 1) + BT , \qquad (10)$$

$$\frac{\partial S}{\partial T} = \frac{A}{\alpha} (\epsilon^{-\alpha} - 1) + C .$$
 (11)

Despite the fact that these forms [(9)-(11)] contain one less free parameter than form (8), their minimum rms deviations fall within 10% of the minimum rms deviation of form (8). The best-fit α values are 0.5, -0.1, and 0.16 for forms (9)-(11), respectively, while the corresponding Néel temperatures are 318.45, 310.25, and 311.95 K.

If one is trying to fit to the two-exponent forms stemming from Eq. (6), one also finds minimum rms values in the same range for the special threeparameter choices:

$$T\frac{\partial S}{\partial T} = \frac{A}{1-y}(\epsilon^{1-y} - 1) - \frac{B}{\frac{1}{2}y}(\epsilon^{-y/2} - 1) , \qquad (12)$$

$$T\frac{\partial S}{\partial T} = \frac{A}{1-y} \epsilon^{1-y} - \frac{B}{\frac{1}{2}y} \epsilon^{-y/2} , \qquad (13)$$

$$\frac{\partial S}{\partial T} = \frac{A}{1-y} \epsilon^{1-y} - \frac{B}{\frac{1}{2}y} \epsilon^{-y/2} , \qquad (14)$$

where $y = \alpha + \gamma$. Note the absence of all explicit background terms. The lowest rms values now correspond to exponents y equal to -0.1, 1.0, and 0.86, respectively, at T_N equal to 310.35, 314.45, and 313.65 K.

For each functional form, the contours of constant rms deviations outline relatively narrow valleys in the exponent-Néel-temperature plane. For a given T_N , the 5% contour includes typically an exponent ± 0.3 and, for a given exponent, T_N is determined to ± 3.0 K.

Inclusion of a background term in the forms (12)-(14) gives improved fits. The functions

$$T\frac{\partial S}{\partial T} = \frac{A}{1-y}(\epsilon^{1-y} - 1) - \frac{B}{\frac{1}{2}y}(\epsilon^{-y/2} - 1) + CT , \quad (15)$$

$$T\frac{\partial S}{\partial T} = \frac{A}{1-y} \epsilon^{1-y} - \frac{B}{\frac{1}{2}y} \epsilon^{-y/2} + CT , \qquad (16)$$

$$\frac{\partial S}{\partial T} = \frac{A}{1-y} \epsilon^{1-y} - \frac{B}{\frac{1}{2}y} \epsilon^{-y/2} + C$$
(17)

give exponents y of -0.7, -0.4, and 1.18, respectively, at T_N equal to 310.15, 310.15, and 311.15 K; form (16) actually gives the smallest rms value of the ten forms tested. This minimum value corresponds to a mean deviation of 0.05 μ VK⁻¹ which is slightly smaller than the estimated uncertainty of our data. Our analysis is thus limited by the accuracy of our data, and we cannot distinguish between the different forms tested. Because of the integration necessary to our analysis, the simplest form of the function we are fitting to, viz., Eq. (8) with no background, has two free parameters in addition to T_N and the exponent. Using the background term BT and C in Eqs. (9)-(11) and (15)-(17), corresponding to a linear temperature dependence of the "normal" thermopower, we compromise between an unsatisfactory background and an excessive number of free parameters. This leads quite naturally to the question of how good the data would have to be such that we could make the distinction between the one-exponent or two-exponent form, or ascribe a value to the exponent. To answer this question, we have generated "perfect" data, assuming a reasonable Néel temperature and exponent, and subjected these data to our fitting procedure. The resulting rms contours have the elongated shape discussed above; from the rms contour corresponding to an accuracy in the data an order of magnitude better than our present data, we estimate that one could determine the exponent to ± 0.1 and T_N to ± 1.0 K.

The final outcome of these fitting procedures can thus be summarized as follows: (i) With the present data one cannot decide which theoretical form is preferred. (ii) If the value of the Néel temperature (i.e., the temperature of the second-order transition) were known exactly (by some other measurement), then the exponent could be determined to ± 0.3 . (iii) Data with ten times the present accuracy would allow a reduction in the uncertainty of the exponent by a factor of 3.

V. DISCUSSION

The wide range in T_N for the different forms reflects the fact that we allowed it to be a completely free parameter. Applying the traditional interpretation to the exponents we can rule out some of the fitting functions: $\alpha + \gamma$ should be 1.0 ± 0.3 and thus the two-exponent fits (12), (14), and (16) give unrealistic exponents. Looking at the one-exponent forms (8)-(11), the resulting exponent may be interpreted either as α as in Eq. (3) or, alternatively, as $\alpha + \gamma - 1$ if $\Delta \sim \epsilon^{28}$ (see Ref. 11). Obviously we cannot distinguish between the two interpretations.

Further discussion hinges on the order of the transition at the Néel point of Cr. Not only does this apparently depend strongly on the purity and thermal history of the sample, ¹⁹ but there are also indications that a first-order transition may look like a second-order transition if the sample has not reached equilibrium, a process which may involve times of the order of 10^5 s.²⁰ The specific-heat measurements of Garnier and Salamon¹⁹ indicate that annealing sharpens the transition and decreases the transition temperature concurrently, and apparently shifts the behavior from second to first order. The anomalous lattice expansion in the vicinity of T_N further complicates the picture. For a sample of the same origin and very similar thermal history (1/L) (dL/dT) is negative in the temperature interval 306 < T < 313 K, which might be the reason why the derivative of our data has its maximum absolute value at a lower temperature than where the kink occurs. Thus the second-order transition would conceivably take place at a higher temperature, but it is interrupted by the first-order transition. We can estimate the extent of the critical region according to²¹

$$\epsilon_c = \frac{1}{32\pi^2} \left(\frac{k_B}{\Delta C}\right)^2 \frac{1}{\xi_0^6} ,$$

where ΔC is the jump in heat capacity per unit volume and ξ_0 is the zero-temperature coherence length. In Cr the problem seems to lie in the choice of ΔC . Salamon *et al.*²² estimate $\epsilon_c \simeq 10^{-2}$, while Garnier and Salamon¹⁹ later quote a ΔC which yields $\epsilon_c \simeq 4 \times 10^{-5}$. Remembering that our temperature difference was of the order of 0.5 K we find that our closest approach to T_N corresponds to $\epsilon_{\min} \simeq 1.7 \times 10^{-3}$; thus it is not clear whether or not we reached the critical region. In Sec. II we have noted the recently proposed relation between thermopower and specific heat, ⁶ Eq. (2). This relation is supposed to hold in the immediate neighborhood of the critical point. It is also a result of the free-electron model, ²³ which rarely applies to critical phenomena. Using the Hall constant $R_H = (n_e e c)^{-1}$, where c is the velocity of light and e the charge of the charge carriers, we can write Eq. (2) in the form²⁴

$$T\frac{\partial S}{\partial T} = (c_{\rm el}^{\rm mag} R_{\rm H} c) / N_a . \qquad (2')$$

This means that $\partial S/\partial T$ and R_H should have the same sign in the vicinity of T_C if this relation between thermopower and specific heat is to hold. In Cr we have seen that $\partial S/\partial T < 0$, but $R_H > 0^{25}$; in Ni $\partial S/\partial T > 0$, but $R_H < 0.^{26}$

Disregarding this difficulty with the sign we can force agreement between our thermopower data and the specific-heat data of Salamon, Simons, and Garnier²² by multiplying the values computed from our data by a factor of order 1/120. As pointed out by Garnier and Salamon¹⁹ the height of the peak in c^{mag} depends strongly on sample preparation, but an increase by a factor of 120 seems unrealistic. For these reasons, we believe that any agreement between c_{el}^{mag} and $T\partial S/\partial T$ is fortuitous. The behavior of S is qualitatively similar to that of the resistivity,²² a connection which also holds in Ni.^{2,6}

As a last point we would like to stress the fact that presently available critical exponents for transport properties which must be measured in the presence of a temperature gradient cannot be taken very seriously, nor can critical exponents which fit data over less than one decade in ϵ . Had we terminated our analysis after fitting to Eq. (8) we could quote a "reasonable" exponent and Néel temperature. However, the other forms, which *a priori* cannot be ruled out, demonstrate that a wide variation of exponents and Néel temperatures is equally "reasonable." With the general lack of knowledge of the background and the large number of free parameters agreement with many functional forms over certain temperature ranges is possible.

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- [‡]Alfred P. Sloan Fellow.
- ¹For a recent review see, e.g., R. D. Parks, AIP Conf. Proc. 5, 630 (1972).
- ²R. C. Zumsteg and R. D. Parks, Phys. Rev. Lett. 24, 520 (1970).
- ³P. P. Craig and W. I. Goldburg, J. Appl. Phys. 40, 964 (1969).
- ⁴I. Nagy and L. Pal, Phys. Rev. Lett. 24, 894 (1970).
- ⁵W. M. McInnes and K. Schröder, in Dynamical Aspects of

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Critical Phenomena, edited by J. I. Budnick and M. P. Kawatra (Gordon and Breach, New York, 1972), p. 305.

- ⁶S. H. Tang, P. P. Craig, and T. A. Kitchens, Phys. Rev. Lett.
- 27, 593 (1971). As for Ni the volume term of the Gibbs-Duhem equation can be shown to make a negligible
- contribution to the chemical potential of Cr. ⁷D. L. Connelly, J. S. Loomis, and D. E. Mapother, Phys. Rev. B 3, 924 (1971).
- ⁸M. E. Fisher and J. S. Langer, Phys. Rev. Lett. 20, 665 (1968).
- ⁹The term "background" is used in the sense of "nondivergent contribution to the quantity under discussion" (such as $T \partial S / \partial T$ or $\partial S / \partial T$).
- ¹⁰M. Ausloos and K. Kawasaki (private communication) (see also Ref. 11).
- ¹¹In this form the theory is a direct extension of the calculations by Suezaki and Mori (Ref. 12) for the anomalous contribution (near T_N) to the resistivity of an antiferromagnet and is based on the assumption that the change in the number of charge carriers is proportional to the band gap Δ which has a temperature dependence $\Delta \sim \epsilon^{\beta}$ (where β is the critical exponent of the magnetization). However, if n should depend on $\Delta^2\simeq\varepsilon^{2\beta}$ [M. Ausloos and K. Kawasaki (private communication)] then the two exponents in Eq. (6) would have the same value, viz., $-(\alpha + \gamma - 1)$.
- ¹²Y. Suezaki and H. Mori, Prog. Theor. Phys. 41, 1177 (1969). ¹³R. Carter, A. Davidson, and P. A. Schroeder, J. Phys. Chem. Solids 31, 2374 (1970).
- ¹⁴J. P. Moore, R. K. Williams, and D. L. McElroy, in

Proceedings of the Eighth Conference on Thermal Conductivity, edited by C. Y. Ho and R. E. Taylor (Plenum, New York, 1969)

- ¹⁵S. Arajs, E. E. Anderson, and E. E. Ebert, Nuovo Cimento B 4, 40 (1971).
- ¹⁶Equation (7) is a good fit to the results of F. J. Blatt and R. H. Kropschot [Phys. Rev. 118, 480 (1960)] for the temperature range of our measurements.
- ¹⁷All fits were done to the integrated forms; this increases the number of free parameters to be determined by one over the number explicitly shown in the differential forms.
- ¹⁸For fits using a large number of data points, $n^{-1/2}$ is the relative standard deviation of the rms value; since we are using n = 120 data points, the 10% criterion is of the order of the standard deviation.
- ¹⁹P. R. Garnier and M. B. Salamon, Phys. Rev. Lett. 27, 1523 (1971).
- ²⁰B. Stebler, C. -G. Anderson, and O. Kristensson, Phys. Scr. 1, 281 (1970).
- ²¹L. Kadanoff et al., Rev. Mod. Phys. 39, 395 (1967).
- $^{22}\mbox{M}.$ B. Salamon, D. S. Simons, and P. R. Garnier, Solid State Commun. 7, 1035 (1969).
- ²³H. M. Rosenberg, Low Temperature Solid State Physics (Oxford, U. P., London, 1963).
- ²⁴M. Ausloos drew our attention to this interpretation.
- ²⁵G. deVries and G. W. Rathenau, J. Phys. Chem. Solids 2, 339 (1957).
- ²⁶J. Smit, Physica (Utr.) 21, 877 (1955).