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Seebeck Coefficient at the Curie Temperature: Specific Heat of Charge Carriers in Ferromagnets*

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(Received 27 May 1971)

The Seebeck coefficient can be related to the specific heat of the charge carriers. Experiments on the itinerant ferromagnet nickel show that the specific heat determined from the Seebeck effect agrees closely with that determined from conventional specific-heat measurements.

Magnetic systems undergoing second-order phase transitions are found to exhibit thermodynamic singularities. While in insulating magnets it is generally found that localized spin Hamiltonians such as in the Ising or the Heisenberg model are adequate for describing most observations of the phase transition, in conducting magnets this is not the case.[1] There is no obvious way to distinguish between localized magnetism and itinerant-electron magnetism.[2] It thus becomes of interest to develop an experimental technique that allows the study of the magnetic ordering of charge carriers.

In several recent investigations of the thermopower of nickel and iron near their Curie temperatures,[3,4] the focus has been on the oscillatory behavior in some samples. In this Letter we report a measurement of the Seebeck coefficient, or equivalently the thermopower, which we interpret directly in terms of the magnetic contribution to the specific heat associated with the charge carriers in nickel. We find that in the case of this extreme itinerant ferromagnet this specific heat is identical to that found in conventional specific-heat experiments. The oscillation in thermopower reported by Nagy and Pal[3] was not observed. This question is examined later. The relation between the Seebeck coefficient and the specific heat was noted many years ago.[5-7]

The experimental technique and interpretation can be understood with reference to Fig. 1. The sample S is connected in a differential thermocouple configuration with platinum reference electrodes R and is mounted isothermally in a vacuum furnace capable of slow temperature scanning. There are four platinum electrodes to permit measurement of sample resistance. A constant temperature difference ΔT, maintained by a separate heater coupled to a temperature controller, is superimposed on an ambient temperature T. The value of ΔT is typically 1°K over a sample length of 3 cm. The thermal potential difference ϵ is measured with nanovolt amplifiers.

In the limit of ΔT small compared to T, the voltmeter reads

$$\epsilon \simeq \frac{\Delta T}{e}\left(\frac{\partial \bar{\mu}_S}{\partial T} - \frac{\partial \bar{\mu}_R}{\partial T}\right). \quad (1)$$

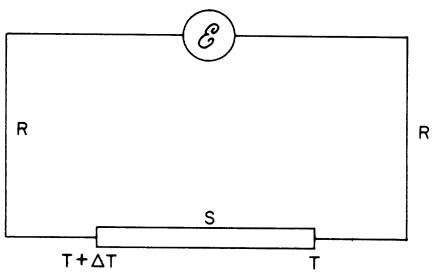

FIG. 1. The thermoelectric circuit is formed from the sample S and reference electrodes R, with a constant temperature difference ΔT.

Here $\bar{\mu}_s$ and $\bar{\mu}_R$ are the electrochemical potentials of the charge carriers in the sample and the reference, respectively. The Seebeck coefficient is thus seen to be proportional to the temperature gradient of the electrochemical potential. The Gibbs-Duhem relation can be used to relate this quantity to the entropy and hence to the integral of specific heat. The Gibbs-Duhem equation for the charge carriers in the metal is

$$d\bar{\mu} = -\mathcal{S}dT - vdp, \tag{2}$$

where $\mathcal{S}$, v, and p refer to the entropy and volume per charge carrier, and to the pressure of the charge carriers. In the measurement the lattice is allowed to expand freely and is described by a known function $v(T)$. We consider the pressure of the electron gas to be a function of the lattice volume and hence of the temperature: $p = q(T)$. For free expansion we have $\varphi = p - q(T) = \text{const}$. Then

$$\frac{\partial\bar{\mu}}{\partial T}\bigg|_{\varphi} = -\mathcal{S} - v\frac{\partial p}{\partial T}\bigg|_{\varphi} = -\mathcal{S} - v\frac{dp}{dT}. \tag{3}$$

Thus the Seebeck coefficient yields the difference in charge-carrier entropy between the sample and reference, plus a pressure correction term which we will show to be small in nickel.

The results for 99.999% pure polycrystalline nickel are shown in Fig. 2. The inflexion point occurring at the Curie temperature is related to the specific-heat maximum.

Upon solving (3) for $\mathcal{S}$, and differentiating, we find the specific heat C_v^e associated with the charge carriers to be

$$C_v^e(\text{sample}) = T\left[\frac{\partial}{\partial T}\left(\frac{\partial\mu_s}{\partial T}\right)_{\varphi v} + \frac{\partial}{\partial T}\left(v\frac{dq}{dT}\right)_v\right] - C_v^e(\text{reference}). \tag{4}$$

The second term in the bracket represents a lattice expansion correction and is $\frac{3}{5}\alpha(\partial\bar{\mu}_s/\partial T)_{\varphi}$ using a free-electron-gas approximation. The coefficient of expansion α of nickel near the Curie temperature is about $10^{-5}\,^{\circ}\mathrm{K}^{-1}$,[8] and $\partial\bar{\mu}_s/\partial T$ is about 50 μV $^{\circ}\mathrm{K}^{-1}$. Thus the expansion correction is less than 1%. The value of C_v^e (reference) is taken as γT with $\gamma(\mathrm{Pt}) = 66\times10^{-4}$ J mole^{-1} $^{\circ}\mathrm{K}^{-2}$ for platinum.[9] For evaluation of the critical contribution, we have also subtracted a linear contribution to the specific heat of nickel with $\gamma(\mathrm{Ni}) = 70.8\times10^{-4}$ J mole^{-1} $^{\circ}\mathrm{K}^{-2}$.[10] The results of differentiating the data of Fig. 2 and making these corrections is shown in Fig. 3. The Curie temperature (633°K) is defined by the maximum in the temperature coefficient of resistance[11] directly measured on this sample. The temperatures found in our experiments have been normalized to yield the same Curie temperature (631.5°K) found by Connelly, Loomis,

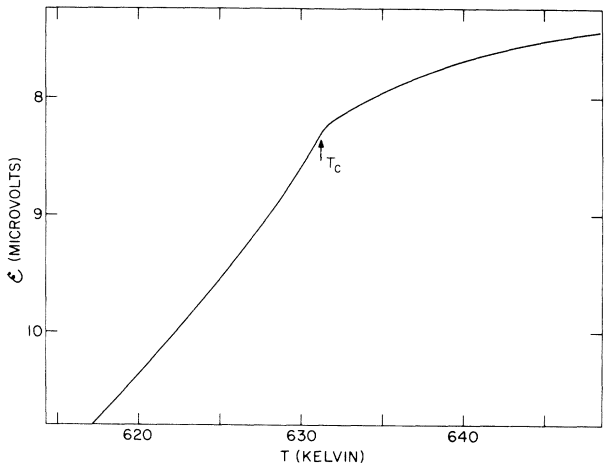

FIG. 2. The Seebeck coefficient of nickel with respect to the platinum reference versus temperature in the vicinity of the Curie point.

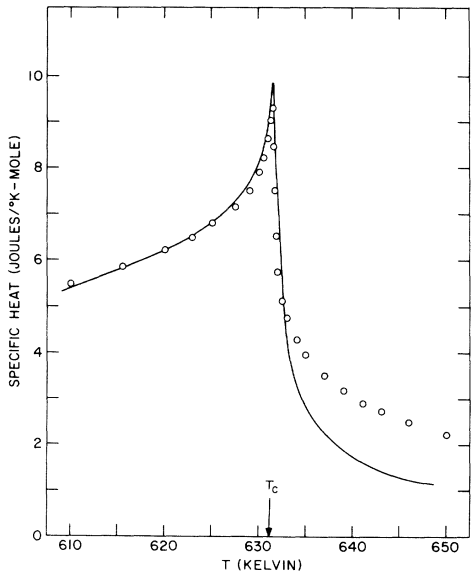

FIG. 3. The magnetic contribution to the specific heat of the charge carriers near the Curie point of nickel. The continuous curve is derived from our Seebeck-coefficient measurements. The points are conventional specific heat as measured by Connelly, Loomis, and Mapother (Ref. 12). The origin of the discrepancy between the two sets of data above T_c is unknown, but may be an experimental artifact. There are no adjustable parameters in either set of data.

and Mapother[12] as indicated by the arrow. For comparison, the critical specific-heat results of Connelly, Loomis, and Mapother are also shown. There are no adjustable parameters involved.

The excellent agreement between the specific heats determined by conventional methods and by Seebeck-coefficient measurements is perhaps not surprising in the case of an extreme itinerant-electron ferromagnet. We have also studied a number of alloys of nickel with copper and with palladium. The results are qualitatively similar to those found in pure nickel, except that the magnetic transitions tend to be broadened. No evidence has been found for the oscillations in thermopower reported by Nagy and Pal.

We speculate that the oscillations reported by these authors result from fluctuations of ΔT which are caused by the magnetic specific heat. A finite temperature difference ΔT produces a distribution of Curie temperatures along the sample. The onset of the specific-heat anomaly is accompanied by a local temperature decrease. To avoid fluctuations in ΔT, measurements would have to be taken in thermal equilibrium. The Nagy and Pal measurements were obtained using a non-steady-state technique. Oscillations qualitatively consistent with Nagy and Pal's results have been observed by us in fast temperature-scanning measurements. This hypothesis avoids recourse to models based upon first-order phase transitions as proposed by Meaden, Geldart, and Sze.[13]

We have also made preliminary measurements on the Seebeck coefficient of iron. The data show oscillations similar to those found by Nagy and Pal, which we attribute to poor temperature and sample homogeneity.

In conducting ferromagnets of a more localized character, it is not obvious that the agreement found in nickel between Seebeck and conventional specific-heat measurements will be found. In order to test this hypothesis, we are at present studying other magnetic ordering systems, such as chromium and the rare earths. In the latter case thermal expansion plays a major role, thereby complicating the interpretation of the results.

The authors have benefited from discussions with D. Brewer, J. Budnick, V. Emergy, and A. Luther.

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*Work performed under the auspices of the U. S. Atomic Energy Commission.

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