

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

P. L. Taylor

Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106

(Received 3 September 1971)

An alternative interpretation is offered of the thermoelectric data of Tang, Craig, and Kitchens.

In a recent paper, by Tang *et al.*¹ some interesting measurements of the Seebeck coefficient of nickel in the vicinity of the Curie point were reported. A comparison with the specific-heat data of Connelly *et al.*² was effected by assuming that the Seebeck coefficient should in general be proportional to the temperature derivative of the chemical potential. Excellent agreement was found below the Curie point T_C , but the two results differed by a factor of about 2 at temperatures greater than $(T_C + 2)$ K. This apparent connection between an equilibrium property and a transport coefficient is particularly startling in view of the fact that transport coefficients are expressible in terms of fluctuations in an equilibrium system, and one would not expect a knowledge of equilibrium averages alone to contain information about such fluctuations. It is thus of crucial importance to decide whether the striking agreement found in Fig. 3 of Ref. 1 is merely fortuitous, or whether it arises as the result of a valid thermodynamic analysis. It is in fact the purpose of this note to question the principal assumption made by Tang *et al.* in analyzing their results, and to suggest an alternative interpretation.

Although the Seebeck coefficient S is conveniently thought of³ as being equal to eS^* , with S^* the "transport entropy per particle," there does not appear to be any valid reason for assuming the identity

$$S^* = - \frac{d\mu}{dT}, \quad (1)$$

with μ the chemical potential that enters the Gibbs-Duhem equation. In fact, the counterexample that springs most readily to mind is that of a superconductor, in which the Seebeck coefficient vanishes, but in which the specific heat remains finite. Alternatively, one might consider the case of the noble metals, in which at most temperatures the Seebeck coefficient and its temperature derivative are strongly positive. Needless to say, the electronic specific heat of neither Cu, Ag, nor Au can be negative, and so Eq. (4) of Ref. 1 is clearly shown to possess no general validity.

It is instructive to examine the physics of thermoelectricity a little further in order to see where

the misunderstanding arises. Let us first consider an experiment in which both ends are cut from a long metal bar at uniform temperature T . One of the two electrically neutral pieces of metal thus obtained is then heated to a temperature of $T + \Delta T$, and the chemical potential μ is thereby altered to a value of $\mu + \Delta T(\partial\mu/\partial T)_N$, the number N of electrons remaining constant during this heating process. The important physical point to note is that this change in chemical potential is in no way related to the Seebeck voltage that would be observed in a thermoelectric experiment. In fact, this change in chemical potential ceases to be directly observable after electrical contact has been made between the pieces (by, for example, connecting them with a superconducting wire), since then sufficient charge will have flowed to render the electrochemical potential uniform in the system.

A completely different result is obtained if first a temperature gradient is produced in the original sample and then the ends are cut off. If, for example, the more energetic electrons from the hot end of the specimen have been less strongly scattered than the less energetic electrons from the cooler end, then an excess negative charge will have accumulated on the cold end of the sample before it is cut off. The consequent voltage difference between the two pieces, neither of which will in general be electrically neutral, will be a true measure of the Seebeck effect. Any changes in chemical potential that occur will again be irrelevant to the voltage measurement.⁴

This reinterpretation eliminates any distress one might have at the divergence of the two curves in Fig. 3 of Ref. 1, where it is seen that around 640 K the magnetic specific heat is approximately twice as great as $T(dS^*/dT)$. One is, however, led to wonder whether something more than coincidence is involved in the close similarity of the two curves at temperatures close to T_C . It is suggestive that in the independent-electron model of thermoelectric effects the Seebeck coefficient is given⁵ by

$$eS = \frac{\pi^2}{3} k^2 T \left(\frac{d \ln \sigma}{d \epsilon} \right)_{\epsilon = \mu}, \quad (2)$$

while⁶

$$-\left(\frac{d\mu}{dT}\right)_v = \frac{\pi^2}{3} k^2 T \left(\frac{d \ln D}{d\epsilon}\right)_{\epsilon=\mu}, \quad (3)$$

with σ the conductivity and D the energy density of states. While the electrons in Ni are by no means independent and the finite compressibility near T_C

should not be ignored, the similarity of the right-hand sides of Eqs. (2) and (3) does tempt one to speculate that the changes in transport properties near T_C are due principally to changes in the density of electronic states.

Conversations with Dr. B. S. Chandrasekhar and Dr. M. E. Fisher are gratefully acknowledged.

*Work supported by the U. S. Atomic Energy Commission.

¹S. H. Tang, P. P. Craig, and T. A. Kitchens, Phys. Rev. Letters **27**, 593 (1971).

²D. L. Connelly, J. S. Loomis, and D. E. Mapother, Phys. Rev. B **3**, 924 (1971).

³C. A. Domenicali, Rev. Mod. Phys. **26**, 237 (1954).

⁴This point is clearly explained by J. M. Ziman [in *Electrons and Phonons* (Oxford U.P., London, 1960), p. 383].

⁵N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Oxford U.P., London, 1936), p. 178.

⁶Reference 5, p. 310.

Reply to "Comment on 'Seebeck Coefficient at the Curie Point Temperature: Specific Heat of Charge Carrier in Ferromagnets'"

T. A. Kitchens

Brookhaven National Laboratory, Upton, New York 11973

and

P. P. Craig

*Brookhaven National Laboratory, Upton, New York 11973
and National Science Foundation, Washington, D. C. 20550*

and

S. H. Tang

*Brookhaven National Laboratory, Upton, New York 11973
and State University of New York, Stony Brook, New York 11790*

(Received 4 October 1972)

INTRODUCTION

Recently, we have attempted a more complete analysis of the critical behavior of the Seebeck coefficient in conducting ferromagnets¹ than was possible in our letter on Ni.² Although we have discussed some of the points raised by Taylor in the previous comment³ in this recent work, we will clarify some of the Taylor's specific points here.

First, contrary to Taylor's introductory remarks, it is now quite generally accepted that it is precisely the same fluctuations which govern the static properties near a critical point that also govern the most accessible of the transport properties, the resistivity.^{4,5} The temperature coefficient of the resistivity has been shown to be closely related to the specific heat in a number of systems.^{6,7}

Second, nowhere in our paper did we relate the chemical potential μ with the "transport entropy"; our Eq. (1) relates the electrochemical potential $\bar{\mu}$ to the transport entropy through a Gibbs-Duhem

relation, and this is *not* equivalent to Taylor's Eq. (1). Indeed, the chemical potential is not related to the Seebeck coefficient by any thermodynamic argument there; it was the purpose of our paper to indicate the strong empirical correlation between the critical component only of these two quantities, and then only when the vdp term is small as is the case for Ni. For other systems, such as Gd along the c axis, the vdp term can dominate the behavior.⁸

Finally, we agree with Taylor that the Seebeck coefficient and the density of states are closely related, but this point is not new. The argument was put forward by Mott⁹ and is referenced four pages after Taylor's Ref. 6. Unfortunately, the calculation only attempts to explain the critical behavior for temperatures below the transition.

In closing, we remark that our new analysis¹ strongly supports the hypothesis of our letter on Ni. The thermoelectric effect can be used to analyze the contribution of the charge carriers to