Diffusion Thermopower of Ferromagnetic Transition metals

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This paper discusses a simple calculation for the diffusion thermopower of a transition metal ferromagnet. The main result of this calculation is that unlike in the case of a free-electron model, the diffusion thermopower \( S \) and its derivative with respect to temperature \( ds/dT \) have opposite signs. The results of this calculation agree qualitatively with experimental results in the high temperature region, where the diffusion thermopower is dominant.

I. INTRODUCTION

Thermoelectric power (TEP) is one of the most well studied transport properties in metals \([1,2]\). It has been shown that it is more sensitive than resistivity to changes in the electronic structure of a material. TEP has one more advantage in that, usually, the sign of the thermopower depends on the sign of the charge carriers as it depends on the electronic charge \( e \), while resistivity is proportional to the square of the charge and hence it has no information on the sign of the charge carriers. At the same time, interpretation of TEP data is complicated by this very sensitivity to the various parameters involved.

The thermoelectric power of a material is usually separated into the diffusion thermopower and the contribution due to ‘phonon drag’ \([1]\). In case of a magnetic material, there are additional contributions due to ‘magnon drag’. It has been shown that the contributions due to phonon and magnon drag are significant only at low temperatures \([1]\). Hence for temperatures higher than the Debye temperature the calculation of the thermopower can be restricted to the diffusion component.

The diffusion thermopower is supposed to be a linear function of temperature, according to the free electron theory of metals \([1]\). In contrast to this, the thermopower of most transition metals is highly non-linear, indicating the inapplicability of the free-electron model to the transition metals.

II. DIFFUSION THERMOPOWER

The TEP results are usually interpreted in terms of the Mott’s formula for diffusion thermopower \([1]\):

\[
S_{diff} = \left[ \frac{\pi^2 k^2 T \, d\ln \sigma}{3e} \frac{dE}{dE} \right]_{E=E_F} \quad (1)
\]

Where \( \sigma \) is the conductivity and \( e \) is the electronic charge. Therefore the thermopower is given by the derivative of the electrical conductivity with respect to energy, evaluated at the Fermi energy.

The electrical conductivity is given by Drude’s formula:

\[
\sigma = \frac{ne^2 \tau}{m} \quad (2)
\]

This equation is based on the free-electron approximation. For transition metals, it is more appropriate to write this formula in the following form:

\[
\sigma(E_F) = \frac{2}{3} e^2 v_s^2 \tau (N_s(E))_{E=E_F} \quad (3)
\]

Where \( \tau \) is the relaxation time and \( N_s \) is the density of states of s-electrons. In the case of transition metals the predominant mechanism for scattering is the scattering of the s electrons responsible for conduction into the less-mobile d states. The relaxation time will be less, if there are more number of d-states available for the scattered electrons. Therefore

\[
\tau = \frac{1}{N_d} \quad (4)
\]

Where \( N_d \) is the density of d-states. Thus,

\[
\sigma(E_F) = A v_s^2 \left[ \frac{N_s(E)}{N_d(E)} \right]_{E=E_F} \quad (5)
\]

where \( A \) is a constant with respect to energy.

In the case of transition metals like Iron it is well known that the density of states has the following form \([1]\):

\[
N_d = N_o (E_o - E)^{1/2} \quad (6)
\]

Where \( E_o \) is the energy corresponding to the top of the d-band. Now using Eq. \([1]\) Eq. \([3]\) and Eq. \([4]\) we get

\[
S = \left[ \frac{\pi^2 k^2 T}{3e} \left( \frac{3}{2E_F} - \frac{d\ln N_d}{dE} \right) \right]_{E=E_F} \quad (7)
\]

Differentiating Eq. \([3]\) we get

\[
\frac{d\ln N_d}{dE} = \frac{-1}{2(E_o - E_F)} \quad (8)
\]

If we substitute this result in Eq. \([7]\) we would get a thermopower which has a negative sign and a linear temperature dependence. Also \( ds/dT \) would have a negative sign, due to the sign of the electronic charge. This is in contrast to experimental results which show that \( ds/dT \) is positive beyond 600°C in the case of Iron \([1]\). To explain these facts we would have to take into account the fact that in a ferromagnetic system, the bands are split
into spin-up and spin-down bands, due to the magnetic interaction. Since there are more electrons in the spin-up band compared to the spin-down band the spin-up d band will be filled to a greater extent than the spin-down band (Fig.1b). Since the chemical potential (Fermi energy) of the two-bands, should be the same, the spin-up band is pushed down with respect to the spin-down band as shown in Fig.1c. Due to this, the number of available d states at $E_F$ is more in the case of the spin-down band than the spin-up band. Hence the electrons will be predominantly scattered into the spin-down band.

Taking both the spin-up and spin-down bands into consideration, we can write,

$$N_+ = N_o(E_1 - E_F)^{1/2}$$  \hspace{1cm} (9)

$$N_- = N_o(E_2 - E_F)^{1/2}$$  \hspace{1cm} (10)

Where $N_+$ and $N_-$ are the density of states at the Fermi surface for the spin-up and the spin-down bands respectively and $E_1$ and $E_2$ are the energies corresponding to the top of the spin-up and spin-down bands respectively (Fig.1c).

Referring to Fig. 1b and Fig.1c, we see that

$$E_1 - E_F = E_o - (E_F + E_\delta)$$  \hspace{1cm} (11)

and

$$E_2 - E_F = E_o - (E_F - E_\delta)$$  \hspace{1cm} (12)

$E_\delta$ is the shift in the Fermi level in the ferromagnetic case with respect to the Fermi energy in the paramagnetic state.

Taking into account both the spin up and spin-down bands, Eq. 9 is rewritten as:

$$S = \frac{\pi^2 k^2 T}{6e} \left[ \frac{1}{(N_+ + N_-)} \left( \frac{dN_+}{dE} + \frac{dN_-}{dE} \right) \right]$$  \hspace{1cm} (13)

Using Eq. 8 and Eq. 10 in Eq. 1, we have

$$S = \frac{\pi^2 kT}{6e} \frac{1}{N_o(E_1 - E_F)^{1/2} + N_o(E_2 - E_F)^{1/2}}$$  \hspace{1cm} (14)

This can be re-written as

$$S = \frac{\pi^2 k^2 T}{6e} \left[ \frac{N_o}{(E_1 - E_F)^{1/2} + N_o(E_2 - E_F)^{1/2}} \right]$$  \hspace{1cm} (15)

Substituting for $E_1$ and $E_2$ we have

$$S = \frac{\pi^2 k^2 T}{6e} \left[ \frac{1}{[(E_o - E_F) - E_\delta]^{1/2}[(E_o - E_F) + E_\delta]^{1/2}} + \frac{\pi^2 k^2 T}{2eE_F} \right]$$  \hspace{1cm} (16)

or

$$S = \frac{\pi^2 k^2 T}{6e} \left[ \frac{1}{(E_o - E_F)^2 - E_\delta^2} \right]^{1/2} + \frac{\pi^2 k^2 T}{2eE_F}$$  \hspace{1cm} (17)

$E_\delta$ can be related to the magnetization in the following manner:

The reduced magnetization is given by:

$$M = \frac{N_+ - N_-}{N_+ + N_-}$$  \hspace{1cm} (18)

Substituting for $N_+$ and $N_-$ and simplifying the expression, we have

$$M = \frac{-E_\delta}{(E_o - E_F) + [(E_o - E_F)^2 - E_\delta^2]^{1/2}}$$  \hspace{1cm} (19)

Rearranging the above equation, we obtain the expression for $E_\delta$ in terms of $M$.

$$E_\delta = -\frac{2M(E_o - E_F)}{1 + M^2}$$  \hspace{1cm} (20)

Substituting Eq. 20 in Eq. 17, we have

$$S = \frac{\pi^2 k^2 T}{3e} \left[ \frac{1}{(E_o - E_F)} \right] \left[ 1 - \frac{4M^2}{(1 + M^2)^2} \right]^{-1/2} + \frac{\pi^2 k^2 T}{2eE_F}$$  \hspace{1cm} (21)

The thermopower is negative at all temperatures, since there is a negative sign from the electronic charge and $E_o > E_F$. This function is plotted in Fig.2 for Iron. The values used for the various quantities are: $E_o - E_F = 1.25eV$ and $E_F = 11.1eV$. Iron has a Curie temperature of $770^\circ C$ which is seen as a peak in the thermopower. Above $T_c$ $M = 0$ and the contribution to the thermopower is only from the second term in Eq. 21. It is seen that $dS/dT$ is positive even though $S$ itself is negative. This is in contrast to the free-electron theory, according to which $S$ and $dS/dT$ have the same sign.

The experimentally measured thermopower for Fe, Co and Ni, fits this model only above the Debye temperature. The maximum seen in the thermopower of Iron at around 200 K has been attributed to magnon drag. However beyond the Debye temperature all these effects are negligible and diffusion thermopower dominates. The minimum seen in the thermopower, may be due to a combination of phonon drag, magnon drag and diffusion components of the thermopower. While the diffusion thermopower has a positive slope between $\theta_D$ and $T_c$, the thermopower due to phonon and magnon drag might have a negative slope. At low temperatures, the phonon and magnon drag dominates over the diffusion part, while at higher temperatures the diffusion thermopower is larger in magnitude. Hence $dS/dT$ will change sign at some temperature near $\theta_D$.

Although Fig.2 matches experimental results quite well in the high temperature region, the magnitude is
slightly greater than what is observed experimentally. According to the theory outlined above, the TEP is of the order of -12 $\mu$V/C at 600 K, but experimental results show that it is of the order of -5 $\mu$V/C or less.

The present approach clearly predicts the experimentally observed peak in the thermopower near $T_c$.

Also it is of interest to note that if the mean field value of $M$ is used in the above equations, one obtains a linear variation for $S$, while if it is assumed that $M \sim ((T_c - T)/T_c)^{0.36}$ according to the Heisenberg model, a non-linear variation of the thermopower is obtained.

### III. CONCLUSIONS

The Thermopower of ferromagnetic transition metals at high temperatures has been interpreted in terms of a simple band picture. It has been shown that the calculated results agree qualitatively with experimental results. Quantitative agreement of the calculated results with experimental results requires the incorporation of phonon and magnon drag effects. Incorporation of these effects is definitely necessary to explain the minimum in the thermopower as well as the thermopower at low temperatures.

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Thermopower (uV/C)

Temperature (C)

Mean Field

Heisenberg