

The thermoelectric power of nickel and its alloys

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The thermoelectric power of nickel and its alloys

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Abstract. Measurements are reported of the temperature variation of the absolute thermoelectric power of pure nickel and its dilute alloys with Pd, Cu, Co, Fe, Mn, Cr, V and Ti. Most of the data have been taken between 2°K and 100°K, although for certain alloys measurements have only been made between 2°K and 15°K. The curves taken over the wider temperature range all exhibit pronounced minima at about 40°K, with the depth of the minima considerably greater in the Ni-Cu, Ni-Co and Ni-Fe alloys than in pure nickel. It is argued that this is due to the effect of spin-mixing on the phonon drag component of thermopower. There is a discussion of the likely influence of spin-mixing on the diffusion thermopower, from which it is concluded that this component of thermopower will exhibit an unorthodox non-linear temperature dependence. However, the magnitude of this effect is considerably smaller than the phonon drag enhancement.

1. Introduction

In two recent papers we have discussed in detail the electrical and thermal conductivities of a number of dilute nickel alloys (Farrell and Greig 1968, 1969 to be referred to as I and II respectively). The interest in those properties arose following the introduction of the concept of spin mixing (see Campbell *et al.* 1967), and this scattering mechanism, unique to ferromagnetic metals, was shown to give rise to unusually large deviations, both from Matthiessen's rule and from the thermal equivalent of the rule.

There therefore seemed every reason to extend the study of these nickel alloys to include the thermoelectric power, particularly as an earlier investigation of this property in a series of Ni-Cu alloys (Greig and Harrison 1965) had shown a rather interesting 'anomaly'; namely the enhancement of an apparent phonon drag peak between the pure metal and the more dilute alloys. It was felt that the interpretation of this phenomenon might also centre on spin mixing.

Consequently we have measured the temperature variation of thermoelectric power of the same specimens as discussed in I and II. For pure nickel and the Ni-Co, Ni-Fe, Ni-Cu and Ni-Pd specimens we have taken measurements between 2°K and 100°K, while for the Ni-Mn, Ni-Cr, Ni-V and Ni-Ti alloys we have concentrated on a rather narrower temperature range, from 2°K to 15°K. The specimens are listed in table 1.

2. Experimental considerations and results

Details of specimen preparation, analysis and mounting have been given in I and II. The thermopower was measured at the same time as the thermal conductivity, with the thermoelectric potential difference ΔV being measured between the same two copper clamps as held the thermocouple thermometers (see II). The absolute thermopower of the copper leads, S_{Cu} , was determined from a comparison with spectroscopically pure lead.

The temperature variation of the absolute thermopower S of the various specimens is shown in figures 1 to 4. The uncertainty in S arises from errors in the measurement of (i) the temperature difference ΔT , (ii) ΔV , and (iii) S_{Cu} . In the case of ΔT the uncertainty is

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Table 1. Details of specimens and experimental low-temperature diffusion thermopower

Nominal composition of alloy (at. %)	Chemical composition (at. %)	Residual resistivity ($\mu\Omega$ cm)	S_a/T ($\mu\text{V deg}^{-2}$)
Pure Ni ^a	—	9.5×10^{-3}	-0.073
+0.3 Pd	0.32	0.045	-0.044
+1 Pd	0.80	0.119	-0.012
+0.3 Cu	0.31	0.247	-0.090
+0.8 Cu ^b	—	0.627	-0.090
+4.9 Cu ^b	—	3.70	-0.092
+1 Co	1.1	0.153	-0.14
+2 Co	2.2	0.297	-0.125
+5 Co	4.7	0.647	-0.10
+0.5 Fe	0.8	0.307	-0.064
+2 Fe	1.8	0.713	-0.10
+5 Fe	4.6	1.80	-0.092
+0.5 Mn	0.48	0.380	-0.090
+0.1 Cr	0.12	0.570	+0.033
+0.1 V	0.12	0.505	+0.016
+0.25 Ti	0.30	0.99	+0.007

a, zone-refined polycrystalline rod supplied by Metals Research Ltd., Royston; b, measured by J. P. Harrison.

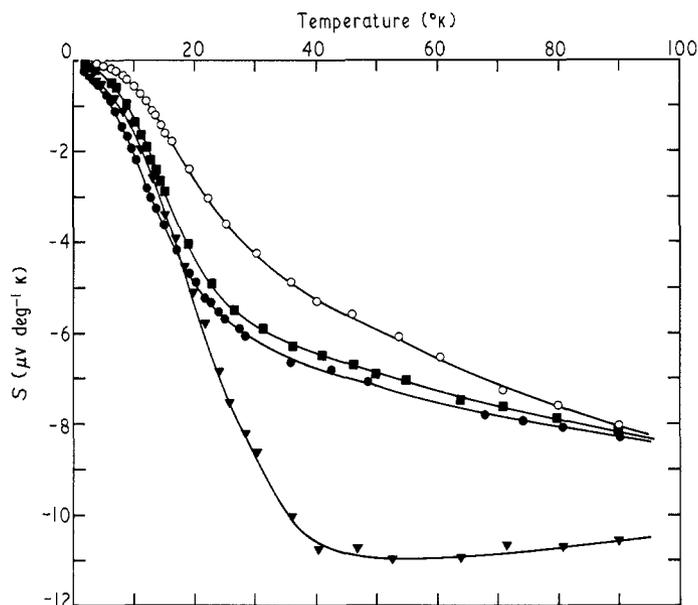


Figure 1. Experimental temperature variation of the absolute thermoelectric power S of pure nickel and the dilute Ni-Pd and Ni-Cu alloys. The symbols represent ● pure Ni; ■ Ni at +0.3 at. %Pd; ○ Ni + 1.0 at. %Pd; ▼ Ni + 0.3 at. % Cu.

approximately 2% over most of the temperature range, although below 5°K the thermometry is rather less accurate leading to an error of about 5%. The magnitude of ΔV varied between alloys in which S was great and those in which it was small. For the results shown in figures 1 and 2, S was quite large, so that even at the lowest temperatures the error in ΔV was about 2%, while over most of the temperature range the uncertainty was about

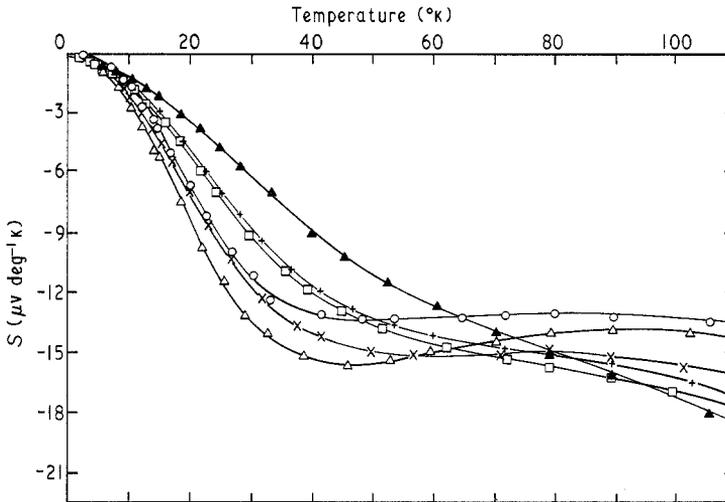


Figure 2. Experimental temperature variation of the absolute thermoelectric power S of the Ni-Co and Ni-Fe alloys. The symbols represent Δ Ni + 1 at. %Co; \times Ni + 2 at. %Co; $+$ Ni + 5 at. %C; \circ Ni + 0.5 at. %Fe; \square Ni + 2 at. %Fe; \blacktriangle Ni + 5 at. %Fe.

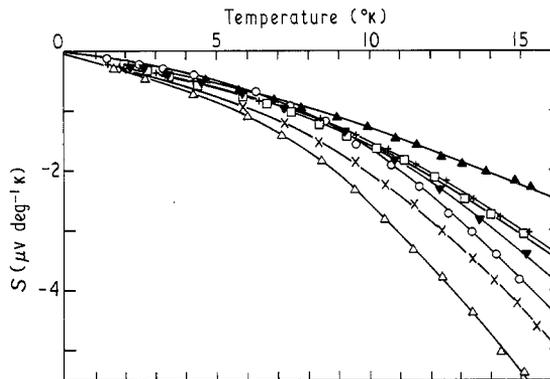


Figure 3. Low temperature detail of the measurements shown in figure 2 and the data on the Ni-Mn alloy. The symbols represent Δ Ni + 1 at. %Co; \times Ni + 2 at. %Co; $+$ Ni + 5 at. %Co; \circ Ni + 0.5 at. %Fe; \square Ni + 2 at. %Fe; \blacktriangle Ni + 5 at. %Fe; \blacktriangledown Ni + 0.5 at. %Mn.

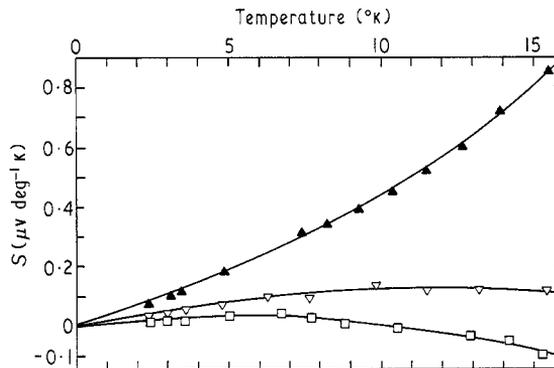


Figure 4. Experimental temperature variation of the absolute thermoelectric power S of the Ni-Cr, Ni-V and Ni-Ti alloys. The symbols represent \blacktriangle Ni + 0.1 at. %Cr; \blacktriangledown Ni + 0.1 at. %V; \square Ni + 0.25 at. %Ti.

0.2%. With these samples S_{Cu} was only of order 0.1S, so that the subtraction of S_{Cu} introduces an error which is negligible. Thus for these samples the total uncertainty in S is about 7% below 5°K and about 2% at high temperatures. On the other hand, in the alloys in which the low-temperature S is very small—that is in Ni–Cr, Ni–V and Ni–Ti— ΔV is very small and the inaccuracy in S_{Cu} cannot be neglected. For these materials the resultant uncertainty could be as great as 20%.

3. Discussion

The overall form of the experimental curves is readily explained. At both ends of the temperature range the measurements vary more or less linearly with T so that at these temperatures the measured thermopower consists almost entirely of the diffusion term S_d . By contrast, at intermediate temperatures the curves exhibit a pronounced minimum, which can be accounted for by the presence of an additional phonon drag term S_g .

However, there is a very noticeable anomaly associated with these minima. On alloying phonons become increasingly scattered by impurities, so that the phonon drag thermopower is normally suppressed. In most of the present alloys the depths of the minima are *greater* than in pure nickel, and S_g appears to be enhanced. We have observed this anomaly before in two earlier series of measurements on Ni–Cu alloys (Greig and Harrison 1965 a, b, Farrell and Greig 1967), but it is now clear that the effect is even more marked in Ni–Co and Ni–Fe. On the other hand, there is no enhancement in the Ni–Pd series.

In our earlier papers we were unable to explain the origin of this enhancement and we must now ask if it is genuinely a phonon drag effect, or if it is perhaps associated with an unorthodox temperature dependence of S_d . In I and II it was reported that large deviations from Matthiessen's rule and the thermal equivalent of the rule exist in alloys of nickel with Co, Fe and Cu. These deviations were interpreted on the basis of a spin-mixing model according to which electrons at high temperatures are continually flipped between spin directions so that the effective resistivities of electrons of opposite spin directions equalize. The high-temperature impurity resistivity can therefore be quite different from the low-temperature residual resistivity; that is to say, Matthiessen's rule is invalid. On the other hand, we also reported in I and II that departures from Matthiessen's rule and its thermal equivalent in Ni–Pd were much smaller and of a different character. Since there is therefore a marked correlation between the magnitude of the deviations from Matthiessen's rule and the depth of the minima in S , it is clear that the explanation centres on spin mixing, and so we first consider possible effects of this on S_d .

3.1. Spin mixing and the diffusion thermopower

At low temperatures the observed diffusion thermopower is determined by impurity scattering processes, so we shall label this $S_{\text{do}}^{\text{LT}}$. Let us assume that in ferromagnetic nickel there are two equal groups of s-like conduction electrons of opposite spin conducting in parallel with impurity conductivities $\sigma_0(\uparrow)$ and $\sigma_0(\downarrow)$. If the thermopowers in these two spin directions are $S_{\text{do}}(\uparrow)$ and $S_{\text{do}}(\downarrow)$ respectively, then (see MacDonald 1962, p. 115)

$$S_{\text{do}}^{\text{LT}} = \frac{\sigma_0(\uparrow) S_{\text{do}}(\uparrow) + \sigma_0(\downarrow) S_{\text{do}}(\downarrow)}{\sigma_0(\uparrow) + \sigma_0(\downarrow)} = \frac{S_{\text{do}}(\uparrow) + r S_{\text{do}}(\downarrow)}{1 + r} \quad (1)$$

where $r = \sigma_0(\downarrow)/\sigma_0(\uparrow)$. At high temperatures, however, owing to spin–spin mixing, the conductivities in the two spin directions equalize, and

$$S_{\text{do}}^{\text{HT}} = \frac{1}{2} \{ S_{\text{do}}(\uparrow) + S_{\text{do}}(\downarrow) \}. \quad (2)$$

Although $S_{\text{do}}(\uparrow)$ and $S_{\text{do}}(\downarrow)$ are both proportional to T , it is clear that $S_{\text{do}}^{\text{LT}}/T$ might be markedly different from $S_{\text{do}}^{\text{HT}}/T$, giving rise to a possible maximum or minimum in the S_{do} against T curves at intermediate temperatures.

However, the analysis of the diffusion term is still not complete. At higher temperatures S_d is determined by intrinsic thermal scattering; let us call this diffusion term S_{di} . The two

components of S_d , S_{d_o} and S_{d_i} are combined according to the Kohler relationship (MacDonald 1962, p. 106).

$$S_d = \frac{W_{e_o}S_{d_o} + W_{e_i}S_{d_i}}{W_{e_o} + W_{e_i}} \quad (3)$$

where W_{e_o} and W_{e_i} are the electronic thermal resistivities attributable to impurity and thermal scattering respectively. If the Wiedemann–Franz law is assumed valid, then (3) may be rewritten as

$$S_d = \frac{\rho_o S_{d_o} + \rho_i S_{d_i}}{\rho_o + \rho_i} \quad (4)$$

where ρ_o and ρ_i are, respectively, the impurity and ideal electrical resistivities.

Under conditions of spin mixing, ρ_o varies with temperature and may be written as $(\rho_o^{L.T.} + \Delta)$, where $\rho_o^{L.T.}$ is the low-temperature residual resistivity and Δ as defined in I gives the deviation from Matthiessen's rule. Since both $\rho_o^{L.T.}$ and Δ are proportional to the impurity concentration c , (4) may be written

$$S_d = \frac{c(\rho_o' + \Delta')S_{d_o} + \rho_i S_{d_i}}{c(\rho_o' + \Delta') + \rho_i} \quad (5)$$

where ρ_o' and Δ' represent the residual resistivity and deviation parameter respectively in a 1 at. % alloy.

On differentiating (5) and letting $c \rightarrow 0$ we find

$$\left(\frac{dS_d}{dc}\right)_{c=0} = \frac{(\rho_o' + \Delta')(S_{d_o} - S_{d_i})}{\rho_i} \quad (6)$$

At high temperatures, where spin mixing is fully effective, S_{d_o} is given by (2) while the value of S_{d_i} is known from measurements on pure nickel. At helium temperatures, $\rho_i \ll \rho_o$, and $S_d \sim S_{d_o}^{L.T.}$. Since r , ρ_o' and $\Delta'(273^\circ\text{K})$ are all known from I, it is clear that (1) and (6) become simultaneous equations for $S_{d_o}(\uparrow)$ and $S_{d_o}(\downarrow)$.

A somewhat similar analysis has been given by Leonard (1968) for the separation of $S_{d_o}(\uparrow)$ and $S_{d_o}(\downarrow)$ except that he did not recognize that the impurity thermopower terms would be spin mixed at higher temperatures, and that ρ_o would be temperature dependent. His expression for $(dS_d/dc)_{c=0}$ is therefore more complicated than (6).

3.2 Numerical estimates of the diffusion thermopower

The diffusion thermopower is proportional to T , while, at low temperatures, the phonon drag contribution is normally proportional to T^3 . Hence

$$S = S_d + S_g = AT + BT^3 \quad (7)$$

in which case it is possible, in principle, to separate the two components from a graph of the low-temperature value of S/T against T^2 . We have obtained A in this way for the alloys in which S was sufficiently large below 15°K to make such a procedure reasonably accurate. For the other alloys, we have estimated A from the data at helium temperatures where S_g is still so small that $S \propto T$. The values of A are collected in table 1.

We see from (5) that when $\rho_o \gg \rho_i$ —that is, at low temperatures— $S_d (= S_{d_o}^{L.T.})$ should be independent of c . This is indeed observed in the Ni–Cu alloys, but for the other types of alloy in which we have measured several specimens, S_d varies through the series. This concentration dependence can be explained if we assume that the pure nickel from which the specimens were made contains an unknown impurity that serves to determine the thermopower in the most dilute alloys. The observed thermopower therefore only tends towards the characteristic $S_{d_o}^{L.T.}$ of any particular alloy series at the higher values of c (assuming that there are no significant changes of band structure over the range of alloying).

The required characteristic thermopower can therefore be obtained from a 'Nordheim-Gorter' plot of S_d/T against $1/\rho_o$, and is the limiting value of S_d/T as $1/\rho_o \rightarrow 0$. The values of S_d/T for the Ni-Co and Ni-Fe series† shown in table 2 have been obtained in this way. In this table we also give values of ρ'_o , $\Delta'(273^\circ\text{K})$, and r , measurements of (dS/dc) at 273°K , and the calculated values of $S_{do}(\uparrow)$ and $S_{do}(\downarrow)/T$.

Table 2. Parameters used in the separation of $S_{do}(\uparrow)$ and $S_{do}(\downarrow)$, and results

Alloy	S_d/T ($\mu\text{V deg}^{-2}$)	ρ'_o ($\mu\Omega\text{ cm}$)	$\Delta'(273^\circ\text{K})$ ($\mu\Omega\text{ cm}$)	r	$(dS/dc)^\dagger(273^\circ\text{K})$ ($\mu\text{V deg}^{-1}\text{ at. \%}^{-1}$)	$S_{do}(\uparrow)/T$ ($\mu\text{V deg}^{-2}$)	$S_{do}(\downarrow)/T$ ($\mu\text{V deg}^{-2}$)
Ni-Cu	-0.090	0.77	0.39	3.7	-1.33	-0.096	-0.089
Ni-Co	-0.090	0.14	0.39	13.2	-0.44	-0.080	-0.091
Ni-Fe	-0.10	0.39	0.55	7.4	-1.33	-0.097	-0.101
Ni-Mn	-0.090	0.79	0.71	5.4	-4.2	-0.19	-0.072
Ni-Cr	+0.033	4.8	3.8	0.21	+30.8	+0.042	-0.0096
Ni-V	+0.016	4.2	0.84	0.42	+19.1	+0.0077	+0.036
Ni-Ti	+0.007	3.3	0.99	0.37	+11.1	+0.023	-0.035

† Values from Köster and Gmöhling (1961).

Also used in the calculation: $\rho_i = 6.30 \mu\Omega\text{ cm}$ (from I), $S_{di}(273^\circ\text{K}) = 18.0 \mu\text{V deg}^{-1}$ (measured by R. J. Dewhurst).

It is clear that although the numerical values of $S_{do}(\uparrow)$ and $S_{do}(\downarrow)$ differ slightly from Leonard's, the overall pattern of the results is very similar, namely that on alloying nickel with elements to its left in the Periodic Table, the impurity thermopowers in both spin directions change from negative to positive close to Ni-Cr. In I we pointed out that the variation of residual resistivity on alloying could be explained on the basis of a virtual bound state passing through the Fermi level. De Faget de Casteljau and Friedel (1956) have shown that in such a situation the diffusion thermopower changes sign, and this is undoubtedly the qualitative explanation of the sign changes. It is interesting to note that the sign change occurs first in the spin \uparrow direction. This is in accordance with the fact that the virtual bound state of higher energy lies in the spin \uparrow direction, and will be the first to cross the Fermi level on alloying. A rather surprising feature of the results is the similarity of the magnitudes of $S_{do}(\uparrow)/T$ and $S_{do}(\downarrow)/T$ in the Ni-Cu, Ni-Co and Ni-Fe series. That is, in the alloys in which the scattering mechanisms in the two spin directions are quite different (as is reflected in the rather large values of r).

Although we believe that the general trend of table 2 is correct, the actual numerical values of $S_{do}(\uparrow)$ and $S_{do}(\downarrow)$ are subject to some uncertainty for the following reasons.

(i) The ice-point may not be a high enough temperature for spin mixing to be fully effective.

(ii) S_d/T may not equal its characteristic value in alloys of which there is only one specimen.

(iii) $(dS/dc)_{c=0}$ is not accurately known for dilute alloys.

(iv) In equating the measured (dS/dc) to (dS_d/dc) we have neglected any possible phonon drag contribution to thermopower at 273°K .

(v) The Wiedemann-Franz law is not strictly obeyed, so that equations (4), (5) and (6) should properly be replaced by their thermal analogues. On this particular point, using data from II, we find that although such a change makes a substantial difference to some of the smaller numerical values of $S_{do}(\uparrow)$ and $S_{do}(\downarrow)$, the overall pattern of the results is quite unchanged.

† Unfortunately we were unable to proceed with the separation of $S_{do}(\uparrow)$ and $S_{do}(\downarrow)$ in the Ni-Pd series because no data are available from which to obtain the ice-point value of (dS/dc) .

In spite of all these difficulties some of the results in table 2 can be accepted with confidence. For example, in the Ni-Co series we see from (1) that, since $r > 10$, $S_{do}(\downarrow)$ must lie close to the measured S_d and is probably known to better than 10%. On the other hand, $S_{do}(\uparrow)$ is strongly dependent on the uncertainties listed and therefore subject to considerably greater error.

Finally, we return to the point as to whether or not the enhanced minima in the S against T curves are a consequence of an unusual temperature dependence of the diffusion thermopower. We note that, irrespective of how (1) converts to (2), the net S_{do} will always be smaller than the greater of $S_{do}(\uparrow)$ and $S_{do}(\downarrow)$. For Ni-Co at 50°K, the maximum possible value of S_{do} is therefore about $-5.0 \mu\text{v deg}^{-1}$. The measured thermopower at that temperature in the most dilute Ni-Co alloy is more than three times that, about $-16 \mu\text{v deg}^{-1}$. Since we believe that $S_{do}(\downarrow)$ for Ni-Co is known to better than 10%, it is clear that the large measured S does not arise from a large S_{do} . So far as the S_{di} is concerned, we do not expect this to change from one specimen to the next, so that although S_{di} may well have an unusual temperature dependence, this cannot explain the enhancement of S on alloying. We conclude that the apparent anomalies cannot be explained in terms of the diffusion component of thermopower.

3.3. Spin mixing and the phonon drag thermopower

Baily (1967) has shown that in a multi-band conductor the overall phonon drag thermopower is given by an expression closely analogous to (1), namely

$$S_g = \frac{\sum_i \sigma_i S_{gi}}{\sum_i \sigma_i} \quad (8)$$

where the suffix i refers to the i th group of carriers. For the present ferromagnetic alloys we therefore adapt the equation to

$$S_g = \frac{\sigma(\uparrow) S_g(\uparrow) + \sigma(\downarrow) S_g(\downarrow)}{\sigma(\uparrow) + \sigma(\downarrow)} \quad (9)$$

We have already pointed out in a short note (Farrell *et al.* 1968) how this equation can be successfully used to explain the overall order of the minima in S . The assumptions were the following.

- (i) At 40°K $S_g(\uparrow)$ and $S_g(\downarrow)$ are not subject to mixing and so remain independent and different.
- (ii) $S_g(\uparrow)$ and $S_g(\downarrow)$ are not substantially changed on alloying.
- (iii) In pure nickel at 40°K the conductivities are determined by electron-electron resistive processes and so are fully mixed with $\sigma(\uparrow) = \sigma(\downarrow)$.
- (iv) For all the alloys at 40°K $\sigma(\uparrow) = 1/\rho_0(\uparrow)$ and $\sigma(\downarrow) = 1/\rho_0(\downarrow)$, with ratios as given in table 2.

From suitably chosen values of $S_g(\uparrow)$ and $S_g(\downarrow)$ it is then possible to use (9) to show the reasons for (i) the enhancement of S_g on alloying; $\sigma(\downarrow)/\sigma(\uparrow)$ is changed from 1 in pure nickel to, for example, 13.2 in Ni-Co; (ii) the depth of the measured minima, which we are now attributing to a phonon drag peak, following the order Ni-Co, Ni-Fe, Ni-Cu; that is, the same order as $\rho_0(\uparrow)/\rho_0(\downarrow)$; (iii) the absence of any enhancement in Ni-Pd; in that series $\rho_0(\uparrow)/\rho_0(\downarrow) \sim 1$.

The modest reduction of $|S|$ on alloying in any one series is caused, partly by the reduction of S_g in the presence of impurities, and partly by the effect of spin mixing on S_d .

In order to account for the behaviour of S_g in this way, $S_g(\downarrow)$ at 40°K must be fairly large and negative, about $-12 \mu\text{v deg}^{-1}$, while $S_g(\uparrow)$ is smaller and positive, about $3 \mu\text{v deg}^{-1}$. Baily (1967) has shown that the sign of S_g is highly sensitive to the shape of the Fermi surface; it is negative if the radius of curvature r_c is positive with respect to the centre of the zone, and positive if r_c is negative. Furthermore, the magnitude of S_g is proportional

to r_c^{-1} . These results have been applied to the noble metals by Bailyn and Dugdale (1967), who show that the positive S_g in these metals originates in the neck region of the Fermi surface. However, in nickel the neck region of the s_{\downarrow} -Fermi surface is considerably narrower and more elongated than in the noble metals, so that there is no contradiction in an $S_g(\downarrow)$ that is large and negative.

The positive sign of $S_g(\uparrow)$ is slightly more difficult to justify. It may be argued that as a positive S_g is observed in Pd and Pt, which, according to Fletcher and Greig (1968) is the result of phonon-induced s - d or d - d scattering, a similar sign would be attached to $S_g(\uparrow)$ since in this spin direction, such scattering processes are possible. However, to consider this in detail, knowledge of the Fermi surface of the spin \uparrow electrons (and holes) is necessary. Although there is abundant theoretical work on this subject, there does not appear to be good agreement with the available experimental observations on the de Haas-van Alphen effect (Tsui 1967).

As a consequence of the signs and magnitudes of $S_g(\uparrow)$ and $S_g(\downarrow)$ there are two remaining points to be made. Firstly, we see from (9) that when $\sigma(\uparrow)$ is greater than about $4\sigma(\downarrow)$, the observed S_g should be positive. According to our analysis in I, $\sigma_0(\uparrow)/\sigma_0(\downarrow)$ is about 5 in Ni-Cr, so, for that particular alloy, we predict a positive S_g . We see in figure 4 that the curvature of the experimental S against T curve is different in the case of Ni-Cr to that in all the other alloys, and this is undoubtedly a clear indication of a positive phonon drag thermopower in Ni-Cr, and a further confirmation of the validity of the spin-mixing model.

Finally, if for Ni-V and Ni-Ti, $\sigma_0(\downarrow)/\sigma_0(\uparrow)$ is about 2.5 as suggested in I, the experimental S_g for both alloys should be fairly large and negative, not too unlike that in Ni-Cu. In fact, when any reasonable estimate of $S_d = AT$ is subtracted from the measured S , the remainder, although still negative, is an order of magnitude smaller than in all other specimens apart from Ni-Cr, and, at 15 °K, is only about $-0.1 \mu\text{V deg}^{-1}$. We conclude that in trying to resolve the ambiguity in the choice of $\rho_0(\uparrow)$ and $\rho_0(\downarrow)$ in I, we incorrectly assigned the calculated resistivities to the wrong direction of spin. The correct ratios of $\rho_0(\uparrow)$ and $\rho_0(\downarrow)$ for Ni-V and Ni-Ti are shown in table 2, so that $\sigma_0(\downarrow)/\sigma_0(\uparrow)$ is 0.42 for Ni-V and 0.37 for Ni-Ti. These amended values of $\sigma_0(\uparrow)$ and $\sigma_0(\downarrow)$ will lead to S_g of the correct order of magnitude.

4. Conclusion

The marked enhancement of the thermoelectric power minima at about 40 °K in dilute Ni-Co, Ni-Fe and Ni-Cu alloys over that in pure nickel is explained in terms of an increase in the phonon drag thermopower. This increase is a consequence of the greater weighting of S_g towards $S_g(\downarrow)$ when the ratio $\sigma_0(\downarrow)/\sigma_0(\uparrow) \gg 1$. There is, in fact, a good correlation between the magnitude of the enhancement and in the values of $\sigma_0(\downarrow)/\sigma_0(\uparrow)$ obtained in I. Furthermore, no enhancement is observed in Ni-Pd alloys in which we estimated $\sigma_0(\downarrow)/\sigma_0(\uparrow) \sim 1$, and a different sign of S_g is observed in the one alloy in which $\sigma_0(\downarrow)/\sigma_0(\uparrow) \ll 1$ (Ni-Cr).

Although we have shown that spin mixing will give rise to an unusual temperature dependence in the diffusion thermopower, the effect will be small and masked by the phonon drag enhancement. Our separation of the impurity diffusion thermopower into components from the two spin directions yields values similar to those obtained by Leonard. In alloys of nickel with its neighbouring elements in the periodic table, $S_{do}(\uparrow)$ and $S_{do}(\downarrow)$ are both fairly large and negative, but on alloying with more electropositive elements these components become smaller and eventually positive. The sign change can be correlated with the presence of a virtual bound state at the Fermi level.

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