LETTER TO THE EDITOR

On the origin of the positive Hall coefficient in disordered TE–TL alloys

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Abstract. We have collected and analysed the available data for the Hall effect and its dependence upon temperature in amorphous Zr–Co, Zr–Ni, Zr–Cu and Ti–Cu alloys. The differences between the measured Hall coefficients, R_H, and the suggested free electron values, R_0, have very similar dependences on the number of electrons in the early transition (TE) metal d band. At temperatures higher than those at which quantum corrections are important, $R_H - R_0$ is either constant (within the experimental error) or decreases slowly with the increasing temperature as the resistivity does. These observations are consistent with the proposition that in these alloys the positive Hall coefficient is due to the spin–orbit effect.

The Hall effect in amorphous alloys has been a subject of considerable experimental and theoretical research during recent years. One of the reasons for this has been the observation that the Hall coefficient R_H is positive in a large number of these alloys. Before this discovery it was generally believed that in non-magnetic amorphous alloys (whose structure is essentially isotropic) the values of the normal Hall coefficient R_0 should be negative and more or less close to the free electron value. In all simple and noble liquid metals and their alloys (whose structure is roughly similar to the structure of amorphous materials), as well as in corresponding amorphous alloys, this is actually the case. In these alloys the deviations in the magnitude of R_H from the free electron value have been explained by the influence of the disordered structure on the magnitude of the electronic density of states, $g(E)$, at the Fermi level E_F [1, 2]. However, during the last ten years it has been established that the positive sign of the Hall coefficient, which is in direct contradiction with the free electron model and its modifications, is quite common in non-magnetic amorphous alloys containing transition metals as their components.

Several approaches have been proposed in order to explain this phenomenon. Probably the most successful explanation of the positive Hall effect in amorphous alloys containing transition metals has been given in terms of the s–d hybridisation. It is well known that the s–d hybridisation strongly affects the electronic properties of these materials. In disordered systems s–d hybridisation leads to the S-shaped dispersion relation $E(k)$ (defined by the peak in the spectral density function $\rho(E, k)$) of the conduction s electrons [3]. The positive sign of R_H occurs when E_F lies within the region of the negative derivative of $E(k)$ with respect to k, i.e. when a negative electron group

velocity occurs [4] and this depends on the alloy composition. Movaghar [5] derived the expression for the transverse conductivity in disordered systems, according to which the sign of R_H is equal to the negative of the sign of $dg(E_F)/dE_F$. Later on Nguen-Mahn *et al* [6] pointed out that the two approaches to the problem of the sign of the Hall coefficient in disordered transition metal based alloys mentioned above are mutually interrelated, since the strong s–d hybridisation simultaneously yields both the S-shaped dispersion relation and the minimum in the electronic density of states.

On the other hand it has been proposed that the positive Hall effect in these alloys is due to the asymmetric scattering of d electrons as is, for example, the case in ferromagnetic materials. A characteristic feature of amorphous ferromagnetic alloys is the very large anomalous Hall effect which arises as a direct consequence of the high resistivity of these materials. It has been argued [7, 8] that in materials with such a high resistivity the anomalous contribution to the Hall effect is mainly due to the so-called side-jump mechanism, i.e. to the lateral displacement which d electrons undergo during the scattering in the presence of the spin–orbit interaction [9, 10]. In this case, the anomalous Hall coefficient R_s is proportional to the square of the resistivity, which is important for our later discussion. Recently, it has been estimated that the strength of the spin–orbit coupling, the magnitude of the valence susceptibility and the high resistivity in non-magnetic amorphous alloys with a positive Hall coefficient are high enough to make a significant contribution to the transverse conductivity, that might actually overcome the normal Lorentz force contribution [11, 12].

In our opinion it is, at the present moment, rather hard to distinguish which one of the effects mentioned above (i.e. s–d hybridisation or asymmetric scattering of electrons) is the origin of the positive Hall coefficient in non-magnetic amorphous alloys. In spite of this and as the problem in question is of the considerable interest, in this letter we reanalyse the available data on the Hall coefficients and discuss our interpretation of the results. In our analysis we have restricted our attention to the Hall effect in amorphous alloys containing early transition (TE) and late transition or noble metals (TL) as their components. Among TE–TL alloys the ones that contain zirconium have been the subject of the most complete investigation and in the following discussion we refer mainly to these particular systems.

The dependence of the Hall coefficient R_H on the alloy composition in amorphous alloys of zirconium with cobalt, nickel and copper is shown in figure 1. The data for R_H are taken from the review paper of Howson and Gallagher [13]. We have also included in figure 1 the new data for R_H in Zr–Co alloys reported by Trudeau *et al* [11] and the data for R_H in liquid cobalt, nickel and copper [14]. In these alloys the Hall coefficient strongly depends on the alloy composition and its sign changes from negative to positive with increasing zirconium concentration. The concentration dependence of R_H in these alloys has already been discussed with respect to their electronic structure [15] and it has been pointed out that the Hall coefficient changes sign for zirconium concentrations which are about 20 at.% higher than those for which Fermi level moves out from the TL d band into the zirconium d band. This fact is, however, consistent with both of the competing interpretations of the Hall effect in these alloys. In order to simplify the problem we have assumed in our analysis that the main reason leading to the positive values of R_H in these alloys is the spin–orbit effect superimposed on the normal Lorentz term, which we have assumed to be equal to the free electron value. Actually, our intention is to see whether such a simplified interpretation can give a reasonable description of the available data.

First we take the normal Hall coefficient R_0 in amorphous zirconium alloys to be approximately equal to the free electron value (as in amorphous alloys of simple and
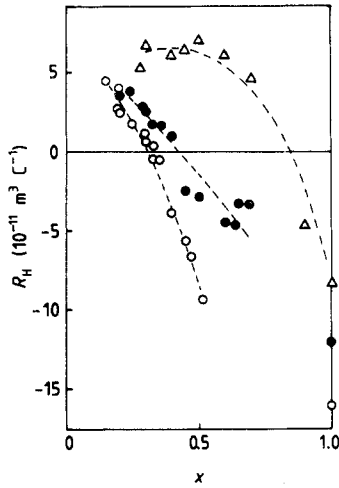
Figure 1. Room temperature Hall coefficients of $Zr_{1-x}Cu_x$ ($\triangle$), $Zr_{1-x}Ni_x$ ($\bullet$) and $Zr_{1-x}Co_x$ alloys ($\bigcirc$).
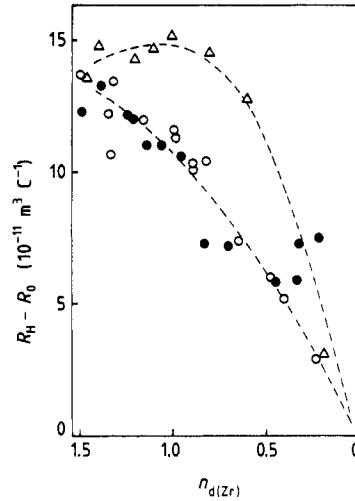
Figure 2. The difference between the Hall coefficient R_H and the corresponding free electron value R_0 as a function of the number of electrons in the zirconium d band $n_{d(Zr)}$ for $Zr_{1-x}Cu_x$ ($\triangle$), $Zr_{1-x}Ni_x$ ($\bullet$) and $Zr_{1-x}Co_x$ ($\bigcirc$) amorphous alloys.

noble metals) that corresponds to the number of s electrons. Here we suppose that the d band contribution to R_0 is, as theory predicts [16] and as is actually the case in liquid nickel, much smaller than the s band contribution. We estimate the value of R_0 in amorphous zirconium, taking into account the atomic volume and the number of s electrons, to be approximately equal to R_0 of liquid copper. Therefore, we assume that in amorphous Zr–Cu alloys R_0 is independent of the actual alloy composition and equal to about -8×10^{-11} m^3 C^{-1}. For amorphous Zr–Ni and Zr–Co alloys we assume that R_0 varies linearly with the zirconium composition starting from -1.2×10^{-11} m^3 C^{-1} and -1.6×10^{-11} m^3 C^{-1} for Ni and Co alloys respectively.

We ascribe the difference between the experimentally determined values of the Hall coefficient R_H and the values estimated above for R_0, $R_H - R_0 = \Delta R_H$, to the spin–orbit effect. Here, ΔR_H should be equal to $R_s \chi$ where χ is the contribution to the magnetic susceptibility corresponding to those electrons that yield the anomalous contribution. We now point out that the anomalous Hall effect in transition metal based alloys is mainly due to the asymmetric scattering of d band electrons [9]. At the same time, as has already been mentioned, the main factor causing the deviations of R_H from the supposed free electron value in Zr alloys which we discuss here is the zirconium d band. For these two reasons, in figure 2 we plot $R_H - R_0$ for the data presented in figure 1 as a function of the number of electrons per atom in the zirconium d band $n_{d(Zr)}$. In the calculation of $n_{d(Zr)}$ we have taken two d electrons per zirconium atom and 0.6 and 1.4 d holes per nickel and cobalt atom, respectively. A somewhat different choice for the number of d holes per nickel and cobalt atom (e.g. 1 and 2, respectively) does not significantly alter the general conclusion concerning the dependence of $R_H - R_0$ on $n_{d(Zr)}$ that can be deduced from figure 2.

The prominent feature of the results shown in figure 2 is that the values of ΔR_H for all three alloy systems coincide both at the highest and the lowest values of $n_{d(Zr)}$.
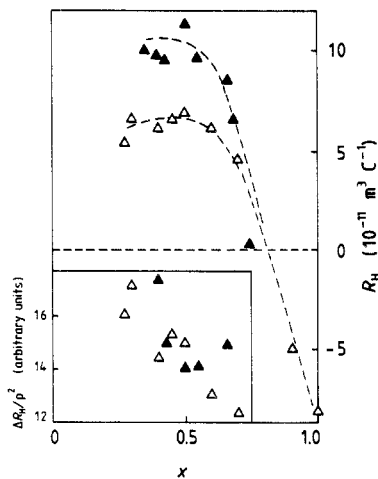
Figure 3. Room temperature Hall coefficients of $Zr_{1-x}Cu_x$ ($\triangle$) and $Ti_{1-x}Cu_x$ ($\blacktriangle$) alloys. Inset: the difference $R_H - R_0$ (for the same alloys) divided by the square of the resistivity.

Moreover, as $n_{d(Zr)}$ tends to zero the values of ΔR_H for all three alloy systems extrapolate to zero. Furthermore, the variations of ΔR_H with $n_{d(Zr)}$ for Zr–Ni and Zr–Co alloys are the same within the dispersion of the original data. An almost linear decrease of ΔR_H with $n_{d(Zr)}$, extrapolating to $\Delta R_H = 0$ for $n_{d(Zr)} = 0$, strongly supports the correlation between the positive R_H in Zr–TL alloys and the Zr d band in these alloys.

Although the values of ΔR_H in Zr–Cu alloys coincide with those for the other two systems at the highest and the lowest value of $n_{d(Zr)}$, the actual variation of ΔR_H is in a way different from that in Zr–Ni and Zr–Co alloys. In particular, ΔR_H in Zr–Cu alloys remains roughly constant down to about $n_{d(Zr)} = 1$ and then decreases very rapidly to zero. At the present moment we have no proper explanation for this difference, but we note that the concentration dependence of the electronic density of states at the Fermi level $g(E_F)$ in Zr–Cu alloys is quite different from that in Zr–Ni alloys. Whereas $g(E_F)$ remains almost constant down to 50 at.% Cu [17] in Zr–Cu alloys, it decreases monotonically with the decrease of Zr content in Zr–Ni alloys [18].

It is interesting to note that the variation of R_H with Cu content seems to be qualitatively the same in all amorphous TE–Cu alloys [4]. (We note that essentially the same variations of R_H have also been observed in liquid Ce–Cu and Pr–Cu alloys [14].) This is illustrated in figure 3 where the variations of R_H with Cu content for the amorphous Ti–Cu and Zr–Cu alloys are shown [13]. Here it may seem that the results presented in figure 3 contradict our proposition regarding the influence of the spin–orbit effect on the Hall effect. This is because the positive contribution to R_H (or $R_H - R_0$) is greater in Ti–Cu alloys, even though Ti is a lighter element than Zr. However, when the values of $R_H - R_0$ in Ti–Cu and Zr–Cu alloys are divided by the corresponding ρ^2 values the difference between the data for two alloy systems tends to vanish within the experimental error, as is demonstrated in the inset of figure 3. This clearly supports the possibility that the spin–orbit effect affects the Hall coefficient in these alloys. A more decisive analysis should take into account the exact values of spin–orbit coupling and the values of the relevant part of the magnetic susceptibility in these alloys, which are, at present, not known to us. (Here, we note that because Zr–Cu, Zr–Ni and Zr–Co alloys have practically the same magnitude of resistivity, the variation of $\Delta R_H/\rho^2$ versus $n_{d(Zr)}$ in these alloys is roughly the same as that of ΔR_H versus $n_{d(Zr)}$ shown in figure 2.) Next, we wish

to show that the temperature dependence of R_H and $R_H - R_0$ (at temperatures higher than those at which quantum corrections to the Hall effect, in particular electron–electron interactions, are important) is consistent with that point of view.

The data for the temperature dependence of R_H at higher temperatures are reported for about twenty amorphous Zr–(Co, Ni, Cu) and Ti–Cu alloys [4, 12, 19, 20]. In all the cases reported, except one (the $Zr_{36}Ni_{64}$ alloy [19]), ΔR_H is either constant (within the experimental error) or decreases slowly with the increase of temperature, regardless of the actual sign of R_H (i.e. if R_H is negative and varies with temperature, its absolute value increases with the increase of temperature). At the same time in these alloys the temperature coefficient of resistivity is small (of the order 10^{-4}) and negative. This eliminates the small possibility that the electron–electron interaction governs the temperature dependence of R_H at higher temperatures. Trudeau *et al* [12] have suggested that the temperature dependence of R_H, particularly in Zr–Co alloys, can be explained by the temperature dependence of the spin–orbit effect, i.e. by the temperature dependence of the valence susceptibility. They have noted that the valence susceptibility in Zr–Co alloys decreases with the increase of temperature and this decrease can lead to the decrease of the anomalous contribution to the Hall effect, i.e. if R_H is negative it leads to an increase in the absolute value of R_H. We note, however, that the more probable explanation for the observed temperature dependence of the Hall effect, which in fact does not compete with the explanation proposed by Trudeau *et al* [12], lies in the temperature dependence of the resistivity. As we have already pointed out, the spin–orbit effect in high resistivity transition metal based alloys should be proportional to ρ^2. If the spin–orbit effect and the temperature dependence of the resistivity are high enough, as they are in some ferromagnetic amorphous alloys below the Curie temperature, it can be observed that R_s does indeed vary with temperature via the ρ^2 dependence [21]. In amorphous zirconium alloys the square of the resistivity decreases, depending on the alloy composition, by about 2–8% in a temperature interval of about 200 K and this decrease is comparable to the relative decrease of the difference $R_H - R_0$. Therefore, we think that the dependence of the spin–orbit effect on the resistivity can account for the observed temperature dependence of R_H. Finally, we would like to emphasise the results reported for Zr–Co alloys [12] and note that for the cobalt concentration close to the one for which R_H changes sign (i.e. for small values of R_H), the relative changes of R_H with temperature are rather high and amount to about 40%. At the same time, the relative changes of $R_H - R_0$ for the same alloys amount to about 3% in agreement with the proposition that the temperature dependence of R_H is due to the temperature dependence of the spin–orbit effect.

In order to summarise what we have pointed out above, we note again that the variations of the Hall coefficient, R_H, in disordered TE–TL alloys are strongly correlated to the position of E_F with respect to the TE d subband. These findings are in qualitative agreement with the approaches based on the effects of the s–d hybridisation as well as those involving the contribution due to the spin–orbit effect. In order to analyse this controversy in more detail, we have corrected the values of R_H in Zr–TL alloys by the expected normal Hall coefficient, R_0 (obtained by a linear interpolation between the observed R_0 of liquid TL and that calculated for Zr due to two s electrons). The so obtained positive value of $\Delta R_H = R_H - R_0$ decreases monotonically as the number of d electrons in the Zr d band, $n_{d(Zr)}$, decreases and vanishes for $n_{d(Zr)} = 0$ in all Zr–TL alloys. Furthermore, the variation of ΔR_H with $n_{d(Zr)}$ is quantitatively the same in both Zr–Co and Zr–Ni alloys. As regards the other TE–TL alloys, it is found that for the same TE content the values of ΔR_H divided by the corresponding squares of resistivity are roughly

the same in both Ti–Cu and Zr–Cu alloys. This is consistent with the contribution of the spin–orbit effect (side-jump mechanism) to R_H of these alloys. Further support for this proposition is obtained from the analysis of the temperature dependence of R_H in amorphous TE–TL alloys. Correlation between the temperature dependence of ΔR_H and that of the resistivity is found to be consistent with the one expected for the spin–orbit effect. In the scope of the analysis presented above, the contribution due to the spin–orbit effect (associated with the d band of TE) appears to be quite a good candidate for the explanation of the positive R_H occurring commonly in disordered TE–TL alloys.

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