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THE HALL EFFECT IN AMORPHOUS ALLOYS OF EARLY AND LATE TRANSITION METALS

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Dedicated to Professor Mladen Paić on the occasion of his 90$^{\mathbf{th}}$ birthday

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We present a detailed analysis of the available data for the Hall effect and its dependence on composition, electrical resistivity and temperature in disordered alloys of early and late transition metals. The systems analysed include amorphous binary Zr-(Co,Ni,Cu), Ta-Ni, Ti-Cu, W-Cu and ternary TE-TL-M alloys (TE = Zr or Ti, TL = Ni or Cu and M = Al or Ga). The results for amorphous La-Ga and liquid Ce-Cu alloys are also included. The dependence of the Hall coefficient on composition, electrical resistivity and temperature indicate that the Hall effect in these systems consists of the normal and anomalous (magnetic) Hall effects that are almost of the same order of magnitude. It is shown that the anomalous contribution is the cause why the Hall effect becomes positive for early transition metal rich amorphous alloys.

1. *Introduction*

Amorphous alloys based on early transition (TE) and late transition (TL) metals are a subject of considerable experimental and theoretical research in more than last ten years. They can often be prepared over wide range of composition, by rapid solidification from the melt, ion-beam mixing, magnetron sputtering etc., which make them suitable for the systematic investigation of the composition dependence of physical properties. However, the understanding of their electrical transport properties develops rather slowly, mainly due to the fact that these alloys have d-states at the Fermi level. One of the problems lacking a general agreement yet is the question of the sign of the Hall coefficient R_H in nonmagnetic TE-TL alloys. In TE-TL alloys R_H is positive in TE rich alloys and negative in TL rich alloys. Obviously, it is strongly dependent on the alloy composition. Before the discovery of the positive Hall coefficient in these alloys it was generally believed that in non–magnetic amorphous alloys (whose structure is essentially isotropic) the values of R_H should be negative and more or less close to the free electron value as in liquid simple and noble metals and alloys.

Today, there are two different (but not mutually exclusive) theoretical approaches to the interpretation of the Hall effect results in disordered TE-TL alloys. According to the first approach, the Hall effect in disordered TE-TL alloys is determined by subtle details of the electronic structure, i.e., by the S-shaped dispersion curve [1,2] or by the minimum in the electronic density of states [3,4] (for a review, see Ref. 5) that are both due to the strong electron scattering and the strong s-d hybridization that are characteristic for transition–metal–based alloys.

According to the second approach, 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 [6,7] 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 [8,9]. In this case, the anomalous Hall coefficient R_S is proportional to the square of the resistivity, that is important for our later discussion. For non–magnetic amorphous TE-TL alloys it has been estimated that the strength of spin–orbit coupling, the magnitude of the valence susceptibility and the high resistivity in these alloys are large enough to make a significant contribution to the transverse conductivity, that might actually overcome the normal Lorentz force contribution [10–12].

In what follows, we demonstrate that the second approach consistently explains the observed dependence of the Hall effect on composition, electrical resistivity and temperature in non-magnetic transition–metal–based alloys. In this presentation, we have included also some R_H data for the disordered alloys based on the light rare earths (RE = La, Ce).

2. Results

In our analysis, we have assumed, as in Ref. 13, that the Hall coefficient, R_H, in non-ferromagnetic TE-TL–based alloys is (as in paramagnetic phase of ferromagnets) equal to the sum of the normal Hall coefficient, R_0, and χR_s, where R_s is the anomalous Hall coefficient and χ is the part of the magnetic susceptibility that corresponds to those electrons that yield the anomalous contribution. Further, we make a rough distinction between s- and d-band electrons. We take the normal Hall coefficient R_0 in TE-TL amorphous alloys to be approximately equal to the free electron value (as in amorphous alloys of simple and 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 [14] and is actually the case in liquid nickel, much smaller than the s-band contribution. The values for R_0 are determined by taking into account the atomic volumes and the numbers of s-electrons of the alloy components [13]. We estimate, for example, the value of R_0 in amorphous zirconium 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 is equal to about -8×10^{-11} $\mathrm{m^3C^{-1}}$. For amorphous Zr-Ni and Zr-Co alloys we assume that R_0 varies linearly with Zr composition starting from -12×10^{-11} $\mathrm{m^3C^{-1}}$ and -16×10^{-11} $\mathrm{m^3C^{-1}}$ for Ni and Co alloys, respectively.

As to the anomalous (i.e., magnetic) contribution to R_H, we consider that it is mainly due to the d-band conduction electrons [8] contributed by TE elements.

To prepare the forthcoming discussion, we emphasize two points. First, we note that the magnetic contribution to R_H is always strongly dependent on the resistivity, ρ. This statement holds regardless of the exact interpretation of the influence of spin–orbit interaction on the electron scattering (i.e., via skew–scattering or side–jump terms [7,9]). Second, we emphasize that in a proper analysis of the magnetic contribution to R_H one actually ought to consider the difference (denoted below as ΔR_H) between the measured R_H and estimated R_0 values.

2.1. The dependence of R_H and $R_H - R_0$ on the alloy composition

First we discuss the dependence of R_H and later that of ΔR_H on the alloy composition.

In TE-based alloys, R_H is positive while in non–ferromagnetic TL-based alloys it is negative, and extrapolates to the free electron value of the host element. Consequently, in TE-TL-based alloys, the sign and the magnitude of R_H depends strongly on the alloy composition. This point is illustrated in Fig. 1 where we show the dependence of the Hall coefficient, R_H, on the alloy composition in amorphous Zr-(Ni,Cu) [5], Zr-Co [5,11], Ta-Ni [15], W-Cu [16] and liquid Ce-Cu [17] alloys. The values of R_H in liquid Ni, Co and Cu [17] are also included. We emphasize the almost identical dependence of R_H on composition in Ce-Cu and Zr-Cu alloys.

The dependence of R_H on concentration in TE-TL alloys has been discussed with respect to their electronic structure [18]. Their electronic density of states (DOS) has a clear structure that can be decomposed into local densities of states (LDOS) for each component of the alloy [19]. The LDOS for TE d-states has a broad peak at higher energies and only a small component at low energies. The LDOS for the other component, TL element, has a broad peak at low energies (i.e., higher binding energies) and only a small component at higher energies. When the concentration of TE element increases the Fermi level shifts from TL d-band to higher energies, i.e., towards the TE d-band. It is instructive to compare the compositions of the alloys for which Fermi level enters the TE d-band with those for which the Hall coefficient changes the sign and becomes positive. In amorphous Zr-(Co,Ni,Cu) alloys the Hall effect changes the sign from negative to positive values at Zr concentrations that are some 20 at% higher than those for which Fermi level moves from predominantly 3-d TL band to the Zr d-band [18]. A similar correlation has been found in amorphous Ta-Ni [15] and V-Al [20] alloys that are, from the chemical point of view, close to the Zr-TL alloys. At the same time, in "pure" TE Ti-V amorphous alloys, R_H is positive for all alloy compositions [21]. In W-Cu alloys however, the tungsten concentration for which R_H becomes positive is significantly high and amounts to about 45 at% [16]. We shall return to this point later on.

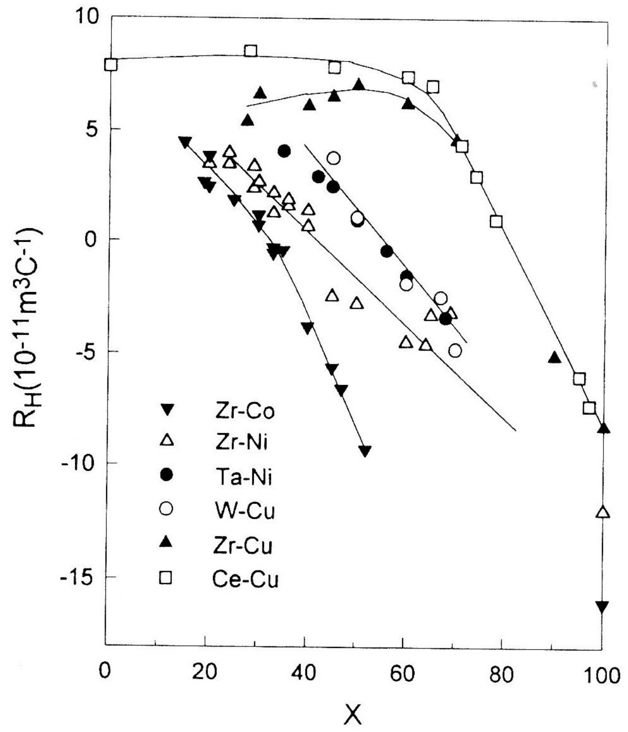

Fig. 1. The Hall coefficient of the amorphous $Zr_{100-x}(Co,Ni,Cu)_x$, $Ta_{100-x}Ni_x$, $W_{100-x}Cu_x$ *and liquid* $Ce_{100-x}Cu_x$ *as a function of* x.

The interpretation of the dependence of the Hall effect on the alloy composition in Zr-(Co,Ni,Cu) and Ta-Ni alloys shown in Fig. 1 becomes rather simple if instead of R_H we look at the $\Delta R_H = (R_H - R_0)$ values as a function of the number of d-electrons in the early transition metal d-band, $n_{d(TE)}$ (Fig. 2). The values for R_0 were estimated as described above. The values for $n_{d(TE)}$ in Zr-(Co,Ni) alloys, for example, have been calculated by taking two d-electrons per zirconium atom and 0.6 and 1.4 d-holes per nickel and cobalt atom, respectively [13]. 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 $n_{d(TE)}$ that can be deduced from Fig. 2.

The prominent feature of the results shown in Fig. 2 is that the values of ΔR_H for Zr-(Co,Ni,Cu) and Ta-Ni alloy systems coincide both at the highest and the lowest values of $n_{d(TE)}$. Furthermore, the variations of ΔR_H with $n_{d(TE)}$ for Zr-Co, Zr-Ni and Ta-Ni alloys are the same within the dispersion of the original data. An almost linear decrease of ΔR_H with $n_{d(TE)}$, extrapolating to $\Delta R_H = 0$ for $n_{d(TE)} = 0$, strongly supports the correlation between the positive R_H in TE-TL alloys and the d-band in these alloys.

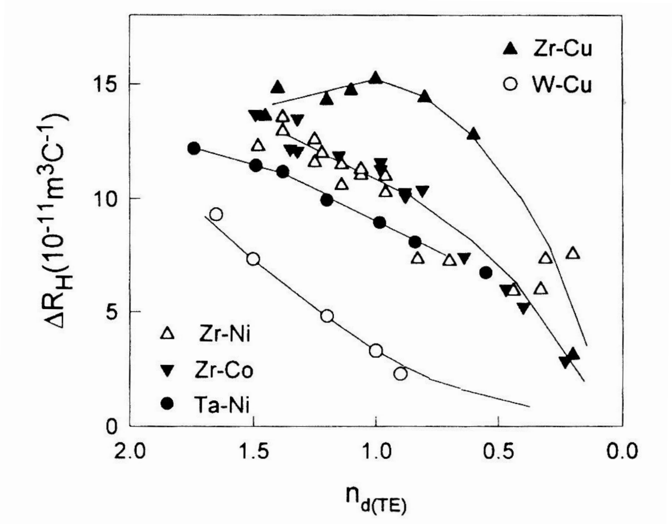

Fig. 2. The difference, ΔR_H, between the Hall coefficient, R_H, and the corresponding free electron value, R_0, as a function of the number of electrons in TE metal d-*band, $n_{d(TE)}$, for* Zr-(Co,Ni,Cu), Ta-Ni and W-Cu *amorphous alloys.*

Although the values of the ΔR_H in Zr-Cu alloys coincide with those for Zr-(Co,Ni) and Ta-Ni systems at the highest and the lowest values of $n_{d(TE)}$, the actual variation of ΔR_H in Zr-Cu is in a way different from that in the alloys with cobalt and nickel. In particular, ΔR_H in Zr-Cu remains roughly constant down to about $n_{d(Zr)} = 1$ and then decreases very rapidly to zero. 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 [22] in Zr-Cu alloys, it decreases monotonically with the decrease of Zr content in Zr-Ni alloys [23].

In W-Cu alloys ΔR_H initially increases significantly slower with $n_{d(TE)}$ than in the four above mentioned alloy systems. Before we propose the possible explanation of this observation, we first note that the magnetic contribution to the Hall effect is strongly dependent on the resistivity of the alloys [7,9]. However, the resistivities of W-Cu alloys [16] are not significantly different from those of Zr-TL [5] and Ta-Ni alloys to explain the weak dependence of ΔR_H on $n_{d(TE)}$ in W-Cu alloys. The lowering of the values ΔR_H on $n_{d(TE)}$ in W-Cu alloys is probably due to the decrease of the spin–orbit coupling parameter λ_{SO}. In fact, it is expected that λ_{SO} (and hence the d-band magnetic contribution), when crossing the periodic table from left to right, decreases and changes the sign for TL. This argument has already been used to explain the opposite signs of the Hall coefficients in amorphous V-Al [20] and Mn-Al [24] alloys with similar transition metal contents.

2.2. The correlation between R_H and electrical resistivity

The magnetic contribution to the Hall coefficient is proportional to either the resistivity or to the square of the resistivity depending on the relative importance of skew–scattering and side–jump terms. The high value of the resistivity of the amorphous alloys and the high strength of the spin–orbit coupling in TE elements are the main causes why the magnetic contribution to RH is so important in amorphous TE-TL based alloys.

In particular, the difference in resistivity between the amorphous Ti-Cu and Zr-Cu alloys almost completely accounts for the difference in their R_H values. In Ti-Cu alloys that contain about 50 at% of copper R_H amounts to about 10×10^{-11} m^3C^{-1} while in Zr-Cu alloys with the similar Cu content R_H amounts to about 6×10^{-11} m^3C^{-1}. However, the values R_H - R_0 divided by the square of resistivities are practically the same (within the experimental error) for the alloys with the same Cu content [13].

The correlation between the electrical resistivity and the Hall effect is particularly noticeable in ternary TE-TL based alloys. In amorphous TE-TL-M alloys (where TE = Zr or Ti, TL = Ni or Cu and M = Al or Ga), the Hall coefficient and the resistivity initially strongly increase on the addition of Al or Ga to the base TE-TL [25–27]. In amorphous $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys R_H increases from 1×10^{-11} m^3C^{-1} for $x = 0$ to 9×10^{-11} m^3C^{-1} for $x = 0.3$. At the same time the resistivity in the same composition interval increases from 180 $\mu\Omega$cm to 230 $\mu\Omega$cm. It is evident that in this case also the increase of the square of the resistivity with the increase of Al content can account for the increase in the magnetic contribution ΔR_H and accordingly can account for the apparently unusually high increase in R_H. On M-rich side, R_H will of course start to decrease and will extrapolate to the values of pure amorphous Al or Ga.

Similarly, in $Zr_2Ni_{1-x}Co_x$ alloys, where resistivity increases somewhat with x, and where R_H is considerably lower for $x = 1$ than that for $x = 0$, R_H shows a shallow maximum around $x = 0.2$. At the same time in $Zr_2Ni_{1-x}Cu_x$ alloys resistivity hardly changes with x and no maximum in R_H as a function of x is observed.

In the next section we will describe how the correlation between the Hall effect and electrical resistivity can explain the observed temperature dependence of the Hall coefficient R_H.

2.3. The temperature dependence of R_H and ΔR_H

The Hall effect in non-magnetic amorphous alloys depends, as expected for isotropic systems, very weakly on the temperature. Here we consider only the temperature dependence of R_H at temperatures higher than those at which the quantum corrections to the Hall effect, in particular electron-electron interaction, are important. The data for the temperature dependence of R_H at higher temperatures have been reported for about thirty amorphous Zr-(Co,Ni,Cu), Ti-Cu, and Ta-Ni alloys [2,11,28-30]. In all cases, except for the $Zr_{36}Ni_{64}$ alloy [28], the temperature coefficient of R_H is either equal to zero (within the experimental error) or is negative regardless of the actual sign of R_H. At the same time, in these alloys the temperature coefficient of resistivity, α, is small (of the order of 10^{-4}) and negative. This eliminates the possibility that the electron–electron interaction governs the temperature dependence of R_H at higher temperatures.

Trudeau et al. [11] suggested that the temperature dependence of R_H, particularly in Zr-Co alloys, is caused by the temperature dependence of the spin-orbit effects, i.e., by the valence susceptibility that decreases with the increase of the temperature. In our opinion, the more probable explanation for the observed temperature dependence of R_H, i.e., ΔR_H, lies in the correlation between the resistivity (that decreases with temperature in alloys considered here) and the magnetic part of the Hall effect. However, because of the weak temperature dependence of both R_H and resistivity, the exact form of this correlation is hard to determine experimentally. In any case, the fact that ΔR_H decreases with the increase of the temperature regardless of the sign of R_H strongly supports our propositions.

We emphasize that, in Zr-Co [11] and Ta-Ni [15] alloy systems, the relative variations of R_H with the temperature are greatest for those alloy compositions for which the Hall coefficient changes sign and is, therefore, very small. In Zr-Co alloys, the relative changes of R_H for small values of R_H are rather high and amount to 40%. At the same time, the relative decrease of $\Delta R_H = R_H - R_0$ for the same alloys amount to about 3% and this decrease is comparable to the decrease of the square of the resistivity. This further indicates that the temperature dependence of R_H actually does not reflect the temperature dependence of the normal Hall coefficient R_0, but that it is actually caused by the temperature dependence of χR_s.

Finally, we mention the temperature dependence of R_H and ρ in amorphous La-Ga alloys with a Ga content between 16 and 26 at% [31,32]. In the alloys with the higher Ga content in which the temperature coefficient of resistivity is negative, R_H significantly decreases with increasing temperature. At the same time, in the alloy with 16 at% Ga, the change of R_H with the temperature is negligible and, actually, this is the alloy with the composition close to that for which the temperature coefficient of resistivity changes the sign. Evidently, the investigation of the temperature dependence of R_H and ρ in the alloy systems in which there is a change of the sign of the temperature coefficient of the resistivity would be very useful.

3. Conclusion

To summarize, 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 TE-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 TE due to two s-electrons). The so obtained positive values of $\Delta R_H = R_H - R_0$ decrease monotonically as the number of d-electrons in TE d-band, $n_{d(TE)}$, decreases and vanishe for $n_{d(TE)} = 0$ in all TE-TL alloys. Furthermore, the variation of ΔR_H with $n_{d(TE)}$ is quantitatively the same in Zr-Co, Zr-Ni and Ta-Ni alloys. The variations of ΔR_H with $n_{d(TE)}$ in W-Cu alloys are slower than in the systems mentioned above. Since we expect λ_{SO} to be depressed around the middle of transition metal series and to change the sign at the other end, the results for W-Cu provide further support to the "magnetic" origin of positive R_H in amorphous TE-TL alloys. Further, it is found that for 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. In the same way, in ternary TE-TL based alloys, the increase of the resistivity with the addition of Al or Ga can account for the strong increase of the Hall coefficient in these alloys. These findings are 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. Accurate measurements of the temperature dependence of resistivity and R_H on the alloys with small positive α (such as $La_{84}Ga_{16}$) would provide a definitive proof of the proposed explanation.

In the scope of the analysis presented above, the contribution due to the spin–orbit effect (associated with the d-band of early transition metal) quite appropriately explain the positive Hall effect occuring commonly in disordered TE-TL alloys, and probably can be applied equaly well to disordered alloys based on light rare earth.

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HALLOV EFEKT U AMORFNIM SLITINAMA RANIH I KASNIH PRIJELAZNIH METALA

Prikazana je detaljna analiza dostupnih podataka za Hallov efekt i njegovu ovisnost o sastavu, električnoj otpornosti i temperaturi u neuređenim slitinama na bazi ranih i kasnih prijelaznih metala. Prikazani su rezultati za amorfne binarne Zr-(Co,Ni,Cu), Ta-Ni, Ti-Cu, W-Cu i ternarne TE-TL-M slitine (TE = Zr ili Ti, TL = Ni ili Cu, i M = Al ili Ga). Priloženi su i rezultati za amorfne La-Ga i tekuće Ce-Cu slitine. Iz ovisnosti Hallovog koeficijenta o sastavu, električnoj otpornosti i temperaturi, zaključili smo da je Hallov efekt u tim sistemima zbroj normalnog i anomalnog (magnetskog) doprinosa. Anomalni Hallov efekt je istog reda veličine kao i normalni i on je uzrok pozitivnog ukupnog Hallovog koeficijenta svojstvenog za amorfne slitine na bazi ranih prijelaznih metala.