The Hall coefficient in Ba–Al alloys

B J Hickey, M A Howson and G J Morgan

Department of Physics, University of Leeds, Leeds LS2 9JT, UK

Abstract. We present the first measurements of the Hall coefficient of a series of BaAl amorphous alloys. The striking feature of the measurements is that the Hall coefficients are *positive* apart from those for the most Al-rich sample and have a strong temperature dependence. We discuss whether the side-jump mechanism or s–d hybridization can account for the sign of the Hall effect in these alloys.

1. Introduction

Studies of the electronic properties of amorphous metals are hampered by the complexities introduced by d-band conduction as most alloys contain transition metals. The attraction of alloys such as $Ca_x Al_{1-x}$ is that the Fermi energy only lies on the edge of the d states due to Ca; thus they have a high resistivity ($\simeq 400\,\mu\Omega$ cm for $x \simeq 0.4$) due to s–d scattering but not such a large number of d states that they make a significant contribution to the conductivity. They also offer the possibility of studying the transition from weak to strong localization. In the liquid state Ba has a much higher resistivity than Ca and the expectation is that amorphous $Ba_x Al_{1-x}$ should give rise to material of very high resistivity on the edge of localization. This indeed turns out to be the case despite the higher spin–orbit interaction of Ba which works against localization. The analysis of the resistivity will be published in the future but the main purpose of this work is to report new results on the Hall coefficient, which is found to be *positive* in Ba-rich samples.

2. Experimental details

Samples were prepared by RF sputtering in an argon atmosphere at a pressure of about 10^{-3} mbar. A target of Al (99.999%) was melted in an argon arc and cut into a disc of 2.5 inches in diameter. Pieces of barium (99.9%) were cut and laid on top of the Al disc. By varying the size and number of pieces the composition of sputtered film could be changed. Typically the target was cleaned by sputtering for about 20 minutes before opening the sample shutter. The films produced in this way were found to be very reactive, and to keep them for the short time necessary to mount them in the cryostat a layer ($\simeq 0.3\ \mu$m) of Si was deposited on the top. This did not interfere with the transport measurements as the room temperature resistance of a test film of silicon was unmeasurable using the sample's four-probe apparatus. Furthermore, for high Al content the samples will survive transfer into the apparatus

without the Si layer, so comparisons between capped and uncapped samples were made and no significant differences found.

The composition of each sample was determined by microprobe and ICP-AES analyses. To measure the sample thickness, a mask was used to cover a slide when sputtering BaAl and removed when sputtering Si. The sample and the Si-alone slide were measured with a DEKTAK surface profiler and hence the sample thickness determined by the difference to an accuracy of about 5%. Samples were usually of the order of a micron thick.

Electrical contact was made by soldering to sputtered Cu or Pt tags. Six contacts were used—two current, two potential and two for the Hall voltage. The samples were mounted perpendicular to a solenoidal field of up to 8 T. Since only two Hall probes were used, the magnetoresistance was measured simultaneously and used to correct the offset produced by imperfect alignment of the two Hall probes. The Hall coefficient is then determined by plotting the corrected Hall resistance against field, the slope of which is $R_{H}t$, where t is the sample thickness. Figure 1 shows two examples of corrected Hall resistances against field.
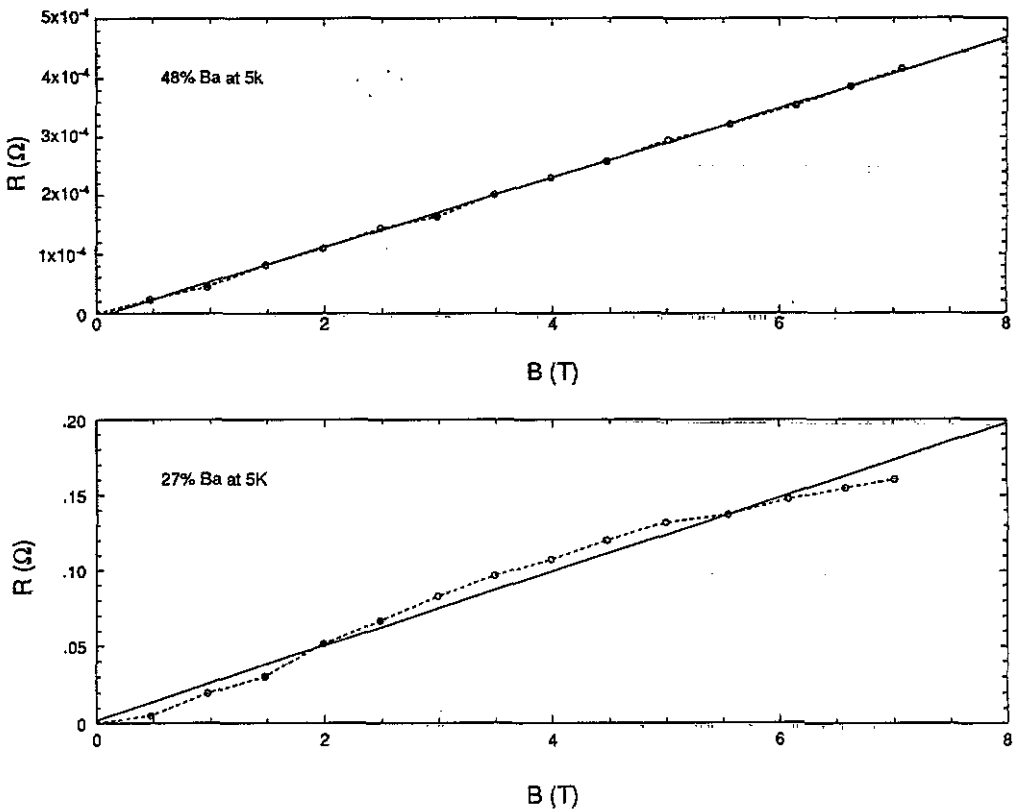

Figure 1. The Hall resistance after correcting for the magnetoresistance of the voltage-probe offset. The top picture shows the best example while the lower is the worst case.

3. Results

Table 1 shows the results for the Hall coefficient and resistivity at 20 K. Note that the Hall coefficient is negative for the 14% Ba sample and positive for the samples of higher Ba concentration. The resistivities are very much higher than most amorphous transition-metal-based alloys, although the samples remain metallic down to the lowest temperature measured (1.5 K). Figure 2 shows the dependence of the Hall coefficient and resistivity on Ba concentration. Where the resistivities are high, the Hall coefficient tends to be large, although we did not observe any clear functional dependence on the resistivity.

Table 1. Hall coefficient and resistivity at 20 K.

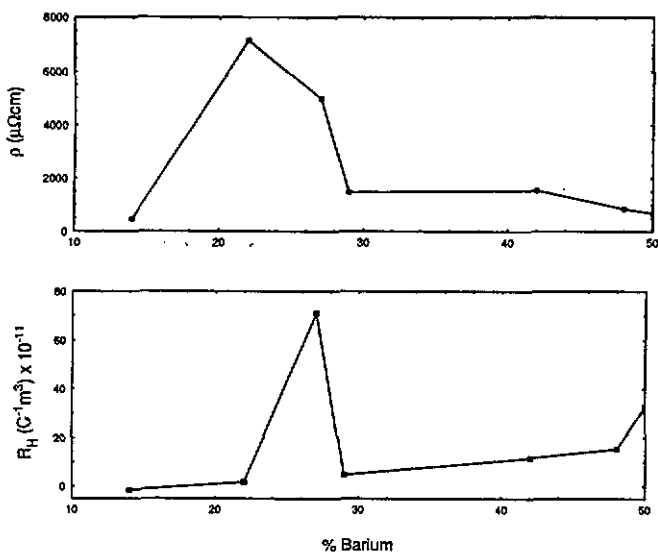| % barium	R_H (10^{-11} C^{-1} m^3)	ρ ($\mu\Omega$ cm)
14	−1.5	450
22	1.8	7162
27	71.0	4975
29	4.8	1467
42	11.7	1537
48	15.4	835
50	32.8	638

Figure 2. The composition dependence of the resistivity and Hall coefficient measured at 20 K.

Figure 3 shows the temperature dependence of R_H for several samples between 1.5 K and 20 K. A surprisingly strong temperature dependence is observed for the highest-resistivity samples whereas the lower-resistivity samples have a much smaller temperature dependence. The Hall coefficient increases by an order of magnitude in one decade of temperature when it is most strongly dependent on temperature.

$$\lambda_{so} = A_{so} I d^2 \sum \frac{(\text{matrix element})^2}{E_n - E_F}.$$
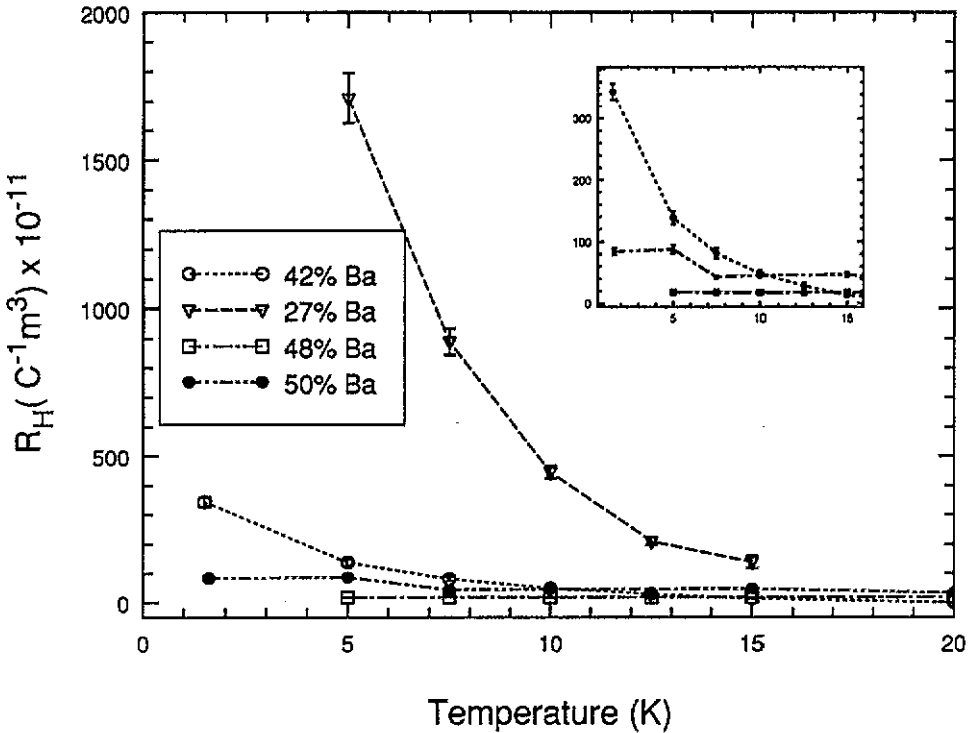
Figure 3. The temperature dependence of the Hall coefficient for various samples. The inset shows the results with an enlarged vertical scale, for all the samples other than the 27% Ba sample.

Here A_{so} is an atomic spin–orbit parameter, I is the overlap integral between atomic orbitals and d is the nearest-neighbour distance. In the paper by Berger and Bergmann [3] the definition of the matrix element is rather ambiguous. It couples states via the angular momentum operator but there is no discussion of the relative role of s- and d-type bands, which is crucial in understanding amorphous transition metals. This form for λ_{so} is claimed to be about 10^4 times greater than the free-electron value and is the key to explaining the large anomalous Hall effect in ferromagnets. It is argued that the sign of λ_{so} depends on the position of E_F in the d band. If E_F is in the lower half of the band, λ_{so} will be positive and if E_F is in the upper half λ_{so} will be negative. This simple picture applies in ferromagnets provided that the spin-up band is full; if not, then contributions from both spin bands must be included. For paramagnetic materials the Hall coefficient can be written as $R_H = R_0 + R_s \chi$ [10] where χ is the susceptibility. R_0 is the normal Lorentz–Hall coefficient and R_s, the anomalous side-jump contribution, equals $2e^2 \rho^2 \lambda_{so} / \mu_0 \hbar \mu_B g$ [10]. If R_s is large and positive compared with R_0, the resultant R_H is positive. It should be noted that R_s is independent of the magnitude or sign of the impurity potential and the mobility of the carriers. For this reason various authors have argued that the d electrons in amorphous transition metals, even though they have a low mobility, can dominate the Hall effect [3, 7, 10, 22]. Note that Weir et al [11] argue that although the d band dominates σ_{xx}, it does not dominate σ_{xy}.

The side-jump argument has been used by some authors [4, 5, 8] to explain the

observation that amorphous alloys containing an early transition metal have positive Hall coefficients or change sign as a function of composition. Many amorphous alloys have relatively small susceptibilities, but this is compensated by the fact that the resistivity enters in squared form. A similar argument should apply to BaAl. As Al is added to these systems, the population of the d band lying just above the Ba Fermi energy, E_F, is increased. There are two competing effects here. There must be sufficient aluminium in the alloy such that E_F for the alloy is in the Ba d band, and there must be sufficient Ba to provide a substantial spin–orbit scattering. It is tempting to say that the observed change in sign as the Ba concentration increases fits this picture; however, there are no susceptibility data for BaAl so further analysis is impossible.

The system CaAl is especially interesting to compare; Ca is isoelectronic with Ba so one expects that the principle differences will be due to the larger atomic number of Ba. The Hall coefficient for CaAl is negative, in spite of some alloys having resistivities as large as 400 $\mu\Omega$ cm. In order to be consistent with the side-jump argument, λ_{so} should be very small. Data from the magnetoresistance [12] show that τ_{so}^{-1}, the spin–orbit scattering rate, is an order of magnitude smaller in CaAl than strong spin–orbit scatterers like CuTi [13] or BaAl. Thus we might expect CaAl to have a free-electron value for the Hall coefficient. In fact both the Hall coefficient and susceptibility are about two to three times larger than free-electron values.

Strom-Olsen *et al* [10] showed that for paramagnetic FeZr plotting R_H against the susceptibility produced straight lines, whose slope provided an estimate of R_s and whose intercept provided an estimate of R_0. Moreover all the alloys considered (between 30% and 37% Fe) had values on the same straight line. Similar curves have been produced by Guntherodt [14] for Co and Bergmann [15] for NiAu. These plots rely on $\rho^2 \lambda_{so}$ remaining constant, which is not true for alloys like CaAl.

Figure 4 shows the data of Mitzutani for CaAl [16] where the room temperature Hall coefficient is plotted against the susceptibility times ρ^2. The slope will now be $2e^2\rho^2\lambda_{so}/\mu_0\hbar\mu_B g$ and we do not expect λ_{so} to vary much between alloys. The slope of the fitted line gives a value for λ_{so} of 6.4×10^{-22} m^2 to be compared with 7.2×10^{-21} m^2 for FeZr. This value is in quite good agreement with expectations. It is an order of magnitude smaller than FeZr, which is expected from the spin–orbit scattering rates estimated from the magnetoresistance. However, the estimate for R_0 is -36×10^{-11} m^3 C^{-1} which is about an order of magnitude greater than a free-electron value. So although the side-jump mechanism may provide an explanation for the composition dependence of R_H, it certainly cannot explain the large value of R_0.

In figure 4 the Hall dependence is dominated by ρ^2 since the susceptibility is nearly constant across the samples. If we do a similar analysis for BaAl we find no correlation between ρ and R_H. This may well be due to a strongly varying χ but this is unlikely.

Let us now consider the arguments and calculations of Howson and Morgan [17] (see also [18]) for amorphous metals composed of transition elements. The first point is that the ordinary conductivity $\sigma_{xx} = \sigma_{yy}$ is dominated by d-band conduction. The Hall coefficient is given by $R_H = \sigma_{xy}\rho^2$ where ρ is the resistivity, and if σ_{xy} is determined by *different* mechanisms to those that determine σ_{xx} we may *always* expect to see a correlation of R_H with the resistivity. The second point is that we have argued that σ_{xy} is determined by a hybridized free-electron band rather than the d states. Calculations for CuZr alloys give a reasonable explanation of the change in sign that occurs with an increasing concentration of Zr. Similar behaviour is observed
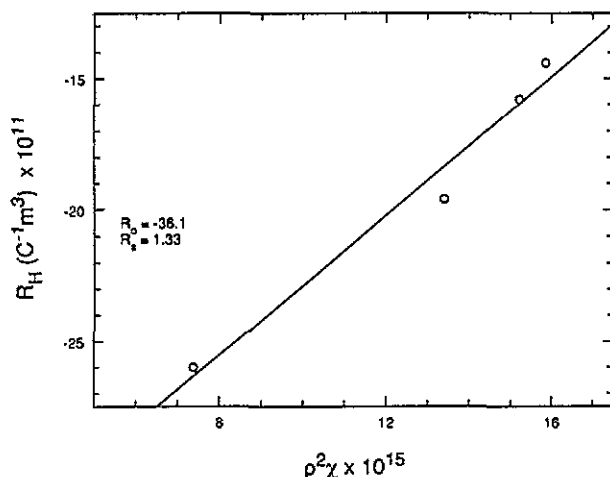
Figure 4. Data for the Hall coefficient of CaAl plotted against the product of the resistivity squared and the susceptibility. The data are from [16].

in CuTi and CuHf alloys, though we should also point out that of the CuTi, CuZr and CuHf alloys the Hall coefficient varies inversely with spin–orbit scattering rates; CuTi has the largest Hall coefficient but the lowest spin–orbit effect. If we now consider CaAl and BaAl alloys we are in a very delicate position where there are not enough d states to carry a large current but where the free-electron-like states will be strongly scattered into the tail of the d density of states and ρ will be very sensitive to the coupling and the position of the Fermi energy. The shift of the Fermi energy into the d states on alloying Ca with Al is a natural explanation of the rapid increase in resistivity in both alloy systems. The behaviour observed in BaAl for R_H is consistent with the s–d hybridization model as the Fermi energy will be close to the point at which a switch over in sign will occur. Nguyen-Manh *et al* [18] derived a simple approximate form for the Hall coefficient $R_H = -\alpha g'(E_F)/2eg^2(E_F)$ where g' is the derivative of the density of states. Here we see that the sign of R_H is determined by the sign of the derivative of the density of states. Hybridization between the s and d bands will reduce the s density of states in the region of the d band and increase the density of states near the *edges* of the d band (see figure 5). If E_F is close to A, then R_H will be negative and greater than the free-electron value (compare CaAl), but if E_F is close to B, R_H will be positive. This behaviour is consistent with what we know about Ca and Ba densities of states [23]. One can argue that the degree of hybridization is larger in BaAl than CaAl but it is very hard to be quantitative in the very delicate interplay between the position of the Fermi energy and the strength of the hybridization. Probably the best way of resolving these issues is by computer simulation similar to those carried out for the ordinary conductivity [19].

There are several possibilities for the source of a temperature-dependent Hall coefficient. Quantum interference effects are very important in materials with such high resistivities. The relative change in the Hall coefficient due to the electron–electron interaction is predicted to have the following form [20]:

$$\Delta R_H(T)/R_H(0 \text{ K}) = -2\Delta\sigma_I(T)/\sigma(0 \text{ K}).$$

The expected temperature dependence at low temperatures (below about 20 K [21])
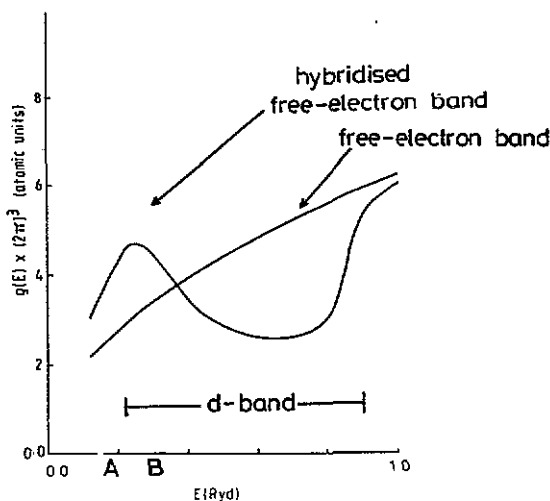
Figure 5. This graph, from [11], is a calculation of the effect of s–d hybridization on a free-electron band. If E_F is near A, then $g'(E)$ is positive, leading to a negative Hall coefficient—and vice versa if it is near B.

is $T^{1/2}$, but this is not the observed temperature dependence for BaAl and the magnitude is much too large.

In the side-jump theory the temperature dependence is given by the product $\rho^2 \chi$; in the case of FeZr [10] ρ^2 was nearly constant, so a very good correlation between the temperature dependence of the Hall coefficient and the susceptibility was found. In our case we do not have data for χ and R_H certainly does not vary as ρ^2. However, we would expect χ to be small and independent of temperature in this paramagnetic alloy.

Schulte *et al* [21] have recently discussed an alternative explanation for the sign of the Hall coefficient in CuTi and CuZr glasses. Their calculation includes the effects of short-range order and s–d hybridization in a two-band model. They find that the sign of R_H can be related to the hybridization between s and d electrons, as first proposed by Weir *et al* [11], and to a finite width in the electronic spectral function. They suggest that the temperature dependence at high temperatures ($T > 25$ K) comes about from thermal broadening of the electron spectral function. At lower temperatures they find that the electron–electron interaction dominates.

We have measured the Hall coefficient as a function of temperature and composition for a series of BaAl alloys. We found a negative Hall coefficient for an aluminium-rich alloy, but as the concentration of Ba was increased the Hall coefficient remained positive up to 50% Ba. The temperature dependence was very strong for some alloys and nearly independent of temperature for others. The current state of theories such as the side-jump and s–d hybridization makes it difficult to apply these arguments to experimental data. It is difficult to state conclusively whether the positive R_H is due to the side-jump or s–d hybridization. However, the strong temperature dependence and the lack of correlation with the resistivity tend to mitigate against the side-jump mechanism.

References

[1] Gallagher B L, Greig D G, Howson M A and Croxon A 1983 *J. Phys. F: Met. Phys.* **13** 119
[2] Berger L 1970 *Phys. Rev.* B **2** 4559
[3] Berger L and Bergmann G 1980 *The Hall Effect and its Applications* ed C L Chein and C R Westgate (New York: Plenum)
[4] Iukov J and Babic E 1990 *J. Phys.: Condens. Matter* **2** 3891
[5] Rhie K, Naugle D G and Bhathnagar A K 1990 *Z. Phys.* B **78** 411
[6] Morel R, Abadli L and Cochrane R W 1990 *J. Appl. Phys.* **67** 5790
[7] Rhie K and Naugle D G 1990 *Phys. Lett.* **149** 301
[8] Iukov J, Babic E and Liebermann H H 1990 *J. Phys.: Condens. Matter* **2** 8591
[9] Fivaz R C 1969 *Phys. Rev.* **183** 586
[10] Trudeau M, Cochrane R W, Baxter D V, Strom-Olsen J O and Muir W B 1988 *Phys. Rev.* B **37** 4499
[11] Weir G F, Howson M A, Gallagher B L and Morgan G J 1983 *Phil. Mag.* B **7** 163
[12] Howson M A, Paja A, Morgan G J and Walker M J 1988 *Proc. 6th Int. Conf. on Liquid and Amorphous Metals (Garmisch, Federal Republic of Germany, 1986); Z. Phys. Chem., NF* vol 2 (Munich: Oldenburg) p 693
[13] Hickey B J, Greig D and Howson M A 1987 *Phys. Rev.* B **36** 3074
[14] Guntherodt J, Kunzi A V, Liard M, Muller M, Muller R and Tsuei C C 1977 *Amorphous Magnetism* ed R A Levy and R Hasegawa (New York: Plenum) p 257
[15] Bergmann G 1976 *Solid State Commun.* **18** 897
[16] Mizutani U and Matsuda T 1983 *J. Phys. F: Met. Phys.* **13** 2115
[17] Howson M A and Morgan G J 1985 *Phil. Mag.* B **51** 439
[18] Nguyen-Manh D, Mayou D, Morgan G J and Pasturel A 1987 *J. Phys. F: Met. Phys.* **17** 999
[19] Hickey B J, Lyon S, Bushnell-Wye G, Finney J, Howson M A and Morgan G J 1990 *J. Phys.: Condens. Matter* **2** 7287
[20] Altshuler B L and Aronov A G 1985 *Electron–Electron Interactions in Disordered Systems* vol 1, ed A L Efros and M Pollak (Amsterdam: North-Holland)
[21] Schulte A, Haensch W, Fritsch G and Luscher E 1989 *Phys. Rev.* B **40** 3581
[22] Trudeau M L and Cochrane R W 1989 *Phys. Rev.* B **39** 13 212
[23] Moriarty J A 1972 *Phys. Rev.* B **6** 4666