The Hall effect in simple glassy structures

The Hall effect in simple glassy structures

Ahmed Houari† and R Harris‡

Centre for the Physics of Materials, and Department of Physics, McGill University, Rutherford Building, 3600 University Street, Montréal, Québec H3A 2T8, Canada

Abstract. We compute the Hall conductivity in a variety of model disordered two-dimensional systems by numerically evaluating the appropriate Kubo–Greenwood formula. Our models range from substitutional binary alloys to topologically disordered 'glasses', and include systems where the disorder is caused by the random small displacements of atoms from their positions in a crystalline lattice. Our Hamiltonian is reminiscent of the Kronig–Penney model in that δ-function-like atomic potentials are specified by a single parameter. We focus particularly on the sign of the Hall coefficient, and establish that the sign can be positive even when there is no well-defined dispersion relation for the electrons. We observe a correlation between the Hall coefficient and the derivative of the density of electron states.

1. Introduction

It is well known that the simple free electron result for the Hall coefficient is $R_H = -1/n \, |e|$, with e the electron charge and n the number density of electrons. The negative Hall coefficients exhibited by simple metals are therefore easy to understand. The positive coefficients observed in other crystalline materials are ascribed to the existence of definite dispersion relations for the electrons, from which are derived negative effective masses.

However, measurements of positive Hall coefficients have also been reported in many liquid and amorphous transition metals, and alloys having transition metal components [1]. Here, since there is no translational invariance of the spatial structure, the concept of an effective mass is of uncertain validity, and so there have been a number of attempts to provide a more appropriate theoretical description.

In its simplest form, the most widely used model of electron transport in noncrystalline metals, namely the Faber–Ziman theory [2], predicts that the Hall coefficient should take its free-electron value. There have thus been various attempts to extend this model. The approach of Weir and co-workers [3] has been to invoke a dispersion relationship and to use the concept of 'effective mass' even when translational invariance is not present. Harris [4] has presented a formula where R_H depends on the derivative of the electron lifetime τ with respect to the energy. His expression explains the positive sign of R_H occuring in many glassy transition metal alloys if $\partial\tau/\partial E$ is large and negative. Such modifications of the Ziman approach require that E_F be

---

† Present address: Unité de recherche de physique, Université d'Oran Es-sénia, 31100 Oran, Algérie.
‡ To whom correspondence should be addressed.

situated in the region of the d-states, as will typically be the case for the transition metal glasses. However, they also require that only weak scattering occurs, and this is certainly wrong in glassy metals.

A quite different approach is based on the experimental observation, first documented by Busch and Guntherodt [5], that the sign of the Hall coefficient is correlated with the sign of the derivative of the density of states, dN/dE. Some time later, Movaghar [6] presented an argument for this idea in the weak scattering limit and suggested that the result might have more general validity. In a more recent approach, Nguyen-Manh *et al* [7] give a justification based on plausible assumptions about the velocity matrix elements between exact eigenstates of the zero-field Hamiltonian. They argue that R_H is proportional to dN/dE, and inversely proportional to the square of $N(E)$ itself, and discuss the relationship of their ideas with those of Weir and co-workers [3].

In this letter, we adopt quite a different approach. We construct models of the topological disorder, and then numerically evaluate the Kubo–Greenwood expression for the Hall coefficient. Our intent is to identify the origins of positive coefficients within the simplest possible model of electronic structure: only then, we believe, can we proceed to model realistic metallic glasses. We show two things, first that there can be a positive Hall coefficient even when the scattering is only s-wave, and when the electron dispersion relation is but poorly defined, and second, that there is indeed a strong correlation with the energy-derivative of the density of electronic states. However, we find that only the extended electron states play a role: to demonstrate these effects within the numerical limitations of our model, we must omit the contribution of those states which are localized.

2. Models of the disorder and of the electronic structure

As in our earlier work on universal conductance fluctuations [8,9], our Hamiltonian is defined in real space in terms of potentials U_i centred at each site R_i of a chosen structure.

The simplest structure is a square lattice, and in this situation the disorder is a consequence of the random distribution of two species of potentials on the sites. Topological disorder is modelled by placing potentials of one species according to structures of close-packed discs with different packing fractions. We use structures generated by a Monte Carlo algorithm [10] with packing fractions appropriate to glassy behaviour. Also, we generate structures in which potentials of one species are displaced from the sites of a square lattice by small random amounts. The x- and y-components of the random displacements are drawn from a rectangular distribution, and the degree of disorder is defined by choosing the width of the distribution. We call these structures 'shaken lattices'[9].

The analytic form of each potential relative to its centre is [11]

$$U(r) = -b e^{-qr} / (1 - e^{-qr})$$

in the limit $b \rightarrow \infty, q \rightarrow \infty$ with $b/q^2 \rightarrow \frac{1}{2}$. This limit is convenient because it determines U by only one parameter γ given by $b = \gamma q + q^2/2$. The potential U then has only one bound state at energy $E = -\gamma^2/2$ with wavefunction $\phi(r) = \sqrt{\gamma/2\pi}\, e^{-\gamma r}/r$ [11]. Although the potential is δ-function-like, it is not a true 3-d δ-function: if it

were, there would be no bound state. Units of energy are such that $\hbar^2/m$ is set to unity, and lengths are measured in terms of the average spacing between sites, which for the crystalline samples is just the lattice spacing.

We then use the set $\{\phi_i(\mathbf{r} - \mathbf{R}_i)\}$ as basis functions for a tight-binding expansion. This yields matrix elements for the Hamiltonian H_0 (in the absence of a magnetic field B) and for the overlap matrix S which has a simple form given in our earlier paper [8]. The tight-binding matrix equations are then solved explicitly for structures containing up to 35^2 sites, giving eigenfunctions of the form

$$\psi_m(\mathbf{r}) = \sum_i a_{mi}\phi_i(\mathbf{r} - \mathbf{R}_i)$$

again for the case when B is zero. It is convenient to use the notation $|m_0\rangle$ for these functions, to distinguish them from the eigenfunctions in the presence of a field, which will be denoted by $|m\rangle$.

3. The Kubo formula for the Hall conductivity

Using the tight-binding wavefunctions, it is straightforward to evaluate the Hall coefficient numerically, using Kubo formulae for the diagonal and nondiagonal elements of the conductivity tensor in a magnetic field B. Thus, in the weak field limit, the Hall coefficient is given by

$$R_{\rm H} = \frac{1}{B}\frac{\sigma_{xy}(B)}{\sigma_{xx}^2}$$

where σ_{xy} denotes the antisymmetric part of the nondiagonal element of the conductivity tensor, and σ_{xx} is the usual diagonal element. To obtain $R_{\rm H}$, σ_{xy} must be calculated to the lowest order in B, i.e. up to $O(B)$, but for σ_{xx} the zero field value is sufficient.

Although the numerical evaluation of the Kubo expression for σ_{xx} has become almost routine [12], there are several possible ways to write the expression for σ_{xy} to simplify its evaluation. The most convenient for present purposes has been given by many authors [13,14] and at $T = 0$ K can be written as

$$\sigma_{xy} = \sigma_{xy}^{\rm I} + O(B^2)$$

where $\sigma_{xy}^{\rm I}$ at energy E is given by

$$\sigma_{xy}^{\rm I}(E) = \frac{i\hbar e^2}{2\Omega}\left\{\sum_m \langle m\,|\,v_x G(E^+)v_y\,\delta(E-H)\,|\,m\rangle - \langle m\,|\,v_x\delta(E-H)v_y G(E^-)\,|\,m\rangle\right\}$$

or in more compact form

$$\sigma_{xy}(E) = -\frac{\hbar e^2}{\Omega}\,{\rm Im}\sum_m \langle m\,|\,v_x G(E^+)v_y\,|\,m\rangle\,\delta(E-E_m)\,.$$

In these expresssions, $E^\pm$ is $E \pm i\eta$, $\eta \to 0^+$, Ω is the volume of the system, and we have used the eigenstates $|\,m\rangle$ of the Hamiltonian H.

All the operators are defined in the presence of the magnetic field, so that the Hamiltonian H contains the appropriate vector potential. Explicitly, we write

$$H = H_0 + iBH_B$$

with

$$iH_B = e(xv_y - yv_x).$$

In terms of H, the velocity operators v_x and v_y are defined as

$$v_z = \frac{i}{\hbar}[H, z] \qquad z = x, y$$

and the resolvent operator is

$$G(E^{\pm}) = 1/(E - H \pm i\eta).$$

To compute R_H requires only terms up to $O(B)$, so that we can write

$$|m\rangle = |m_0\rangle + B|m_B\rangle$$
$$v_x = v_x^0 + Bv_x^B$$

and

$$G = G^0 + iBG^0 H_B G^0.$$

Of the terms which result from the corresponding substitutions, we keep only those of $O(B)$, and those terms which have the correct symmetry under the exchange of x and y coordinates. We then obtain

$$\sigma_{xy}^I = -\frac{\hbar e^2}{\Omega} B \operatorname{Re} \sum_m \langle m_0 | v_x^0 G^0(E^+) H_B G^0(E^+) v_y^0 | m_0 \rangle \delta(E - E_m).$$

The final simplification is the neglect of the real parts of $G^0(E^+)$ which we justify in the same manner as do Morgan *et al* [14], so that we obtain

$$\sigma_{xy}^I = \frac{\hbar e^2}{\Omega} B \sum_m \langle m_0 | v_x^0 g^0 H_B g^0 v_y^0 | m_0 \rangle \delta(E - E_m)$$

where the imaginary part of G^0 is written as

$$g^0(E) = \pi\delta(E - H_0).$$

This is an expression which can be evaluated with the knowledge of only the eigenvalues and eigenfunctions of the zero-field Hamiltonian H_0. It is convenient to evaluate the matrix elements of H_B by expressing them in the form given by Bhattacharya *et al* [15].

In the actual computation, we must compensate for the discreteness of the energy spectrum of our finite systems by giving each delta function a finite width ϵ [8]. Therefore σ_{xy} and σ_{xx} are given by

$$\sigma_{xx}(E) = \frac{\hbar e^2}{\Omega} \frac{1}{\epsilon^2} \sum_{n,m}' |\langle m_0 | v_x | n_0 \rangle|^2$$

$$\sigma_{xy}(E) = \frac{2\pi^3}{\Omega} \left(\frac{e^2}{h}\right) \frac{1}{\epsilon^3} \sum_{l,m,n}' \langle l_0 | [H_0, x] | m_0 \rangle \langle m_0 | H_B | n_0 \rangle \langle n_0 | [H_0, y] | l_0 \rangle$$

where the primed sums extend only over states within a window of width ϵ around the energy E. In our calculations ϵ is taken to be approximately 2% of the total bandwidth.

4. Results

Representative results of the calculation of σ_{xy} as a function of energy are shown in figure 1, and the corresponding Hall coefficients R_H in figure 2. In each case the data shown are averages over 10 runs, and the statistical variation from the mean values at each energy is around 0.5×10^{-3} units for σ_{xy} and around 0.1 units for R_H. The first data, obtained for purposes of comparison, refers to substitutional alloys on a square lattice with 35^2 sites. 90% of the sites have $\gamma = 1.0$, and the remainder have $\gamma = 1.5$. The variation of the sign of R_H as a function of energy is clearly evident, with a change of sign occuring roughly in the middle of the band. The units are such that the 'free-electron' value would be unity. These data can be understood in terms of the electron dispersion relation, which is well defined, and has an inflection point precisely at the energy where R_H changes sign. The numerical procedure is thus successful in this situation.
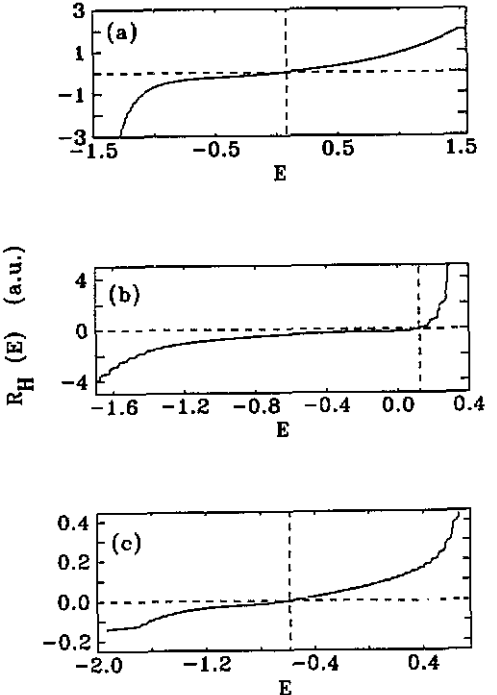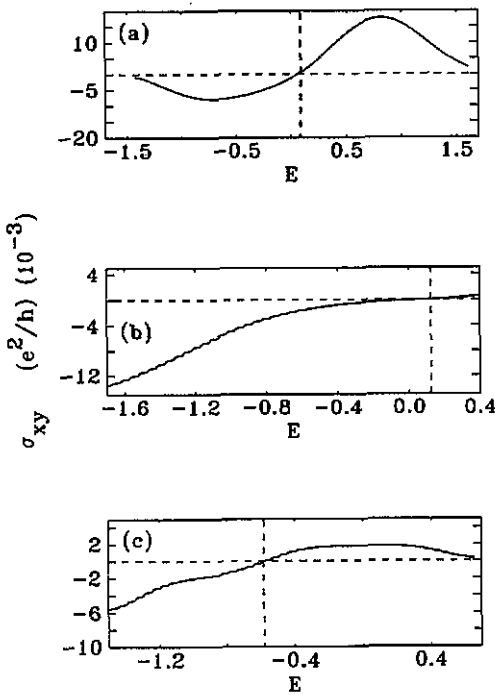

Figure 1. The off-diagonal conductivity for unit field, $\sigma_{xy}(B)$ $B = 1.0$, as a function of energy for three different disordered systems: (a) substitutional alloy (b) topological disorder (c) shaken lattice. For details of the structures, see the text. The broken lines intersect where σ_{xy} changes sign.

Figure 2. The Hall coefficient R_H as a function of energy for three different disordered systems: (a) substitutional alloy (b) topological disorder (c) shaken lattice. For details of the structures, see the text. The broken lines intersect where R_H changes sign.

The second data set is for topologically disordered systems. They are the same structures, with packing fraction 0.64, used in our investigation of conductance fluctuations [9]. The change in sign of σ_{xy} as a function of energy is still present, although

no longer at the centre of the band, but the variation of R_H with energy shows large variations at the edges of the band. These can be traced to small values of σ_{xx} caused, in their turn, by the presence of localized states. These states are identified both by the values of their participation ratios [16] and, in some cases, by visual inspection of their spatial distribution.

Also shown in the figures are data for shaken lattices with random displacements chosen from a random distribution with maximum value 20% of the lattice spacing. The degree of disorder in these systems is comparable to that in the topologically disordered systems, as measured at the centre of the band both by a participation ratio of around 0.26, and by a conductivity σ_{xx} of around 5.0 units [9]. Once again, there is a clear indication of a change in sign of σ_{xy} as a function of energy: it occurs near the centre of the band. As for the topologically disordered case, the Hall coefficient R_H diverges at the edges of the band, because of the presence of localized states.

The existence of the change of sign of σ_{xy} in all three cases is our first important result. Positive Hall coefficients arise from s-wave scattering alone, both in substitutionally and topologically disordered situations. We have explicitly verified that this not because of a vestigial dispersion relation $E(k)$. A Fourier analysis of typical wave functions at energy E shows that they are a superposition of all possible plane waves having that same energy. It is therefore of interest to investigate possible correlations with other physical parameters.

In this respect, our next result is the observation that the Hall conductivity σ_{xy} changes sign at the energy where the density of states happens to have a maximum. In particular, this is the case both for the shaken lattices and for the topologically disordered systems, although for these latter systems, the positive value of the Hall conductivity is very small, and occurs over only a restricted range of energy. This observation is consistent with an association of the Hall coefficient with the derivative of the density of states: an association that can be tested numerically.

Because numerical differentiation of our density of states functions is an inherently noisy procedure, we choose to integrate the Hall coefficient to give $N_H(E) = -\int R_H(E)dE$ and then plot $N_H(E)$, suitably normalized, and $N(E)$ against energy for the three sets of data. The results are shown in figure 3, and the agreement between the two sets of curves is remarkable, particularly if we ignore energies near the lower band edge. This is a legitimate omission, since from our previous work [8,9] we know that in this region the electron states are strongly localized. The degree of localization, as measured by the participation ratio, increases dramatically as the energy approaches the band limit, and there is even some evidence for a mobility edge.

In view of the suggestion of Nguyen-Manh *et al* [7] that R_H is also inversely proportional to the square of $N(E_F)$ itself, we have also compared $N(E)$ against $-\int N(E)^2 R_H(E)dE$. Since $N(E)$ varies only gradually with energy in the central regions of our bands, the agreement in these regions is equally good. However, in regions close to the upper band edges, where $N(E)$ varies strongly with energy, agreement is significantly worse. We do not find conclusive evidence, therefore, to support their suggestion.

5. Discussion

The reason for the striking correlation between R_H and the density of states is far from clear, although in principle it must depend upon the properties of the matrix elements
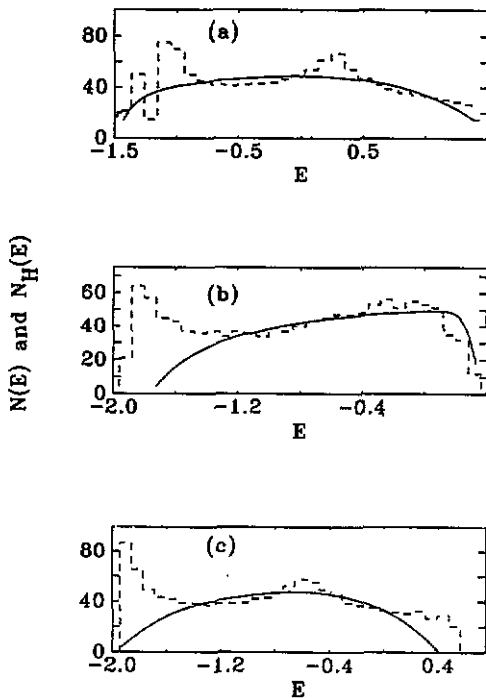
Figure 3. The integrated Hall coefficient $N_H(E)$ (full curves), and the density of states $N(E)$ (broken curves) as a function of energy for three different disordered systems: (a) substitutional alloy (b) topological disorder (c) shaken lattice. For details of the structures, see the text.

of the velocity operators v_x and v_y. Our numerical data suggests that these matrix elements—at least between states that are close in energy—are essentially random variables, but we have not been able to characterize their distribution in a meaningful way. Thus, we have not yet succeeded in reducing the analytic expression for σ_{xy} to a form which transparently reproduces our numerical results.

In this respect we have not been able to improve upon the work of Nguyen-Manh *et al* [7]. As their discussion makes clear, in order to develop a suitable decoupling procedure, it is important to take account of the correlations between the velocity matrix elements of states which are close in energy. Presumably these correlations have to do with the nature of the wavefunctions themselves, and will emerge from a detailed study of the subtle real-space correlations in the strong scattering regime. We intend to carry out such a study in the context of extensions of 'weak localization' theory to this regime [17] using the simple numerical models described in this paper. It will then be possible to study the role of the localized states near the band edge, and to improve understanding of the velocity matrix elements and of the mechanisms for electron transport in a magnetic field.

Acknowledgments

References

[1] A review of data for liquid metals can be found in Kunzi H U and Guntherodt H J 1980 *The Hall Effect and its Applications* ed C L Chien and C R Westgate (New York: Plenum) p 215
    A recent review of the data for glassy metals is found in Howson M A and Gallagher B L 1988 *Phys. Rep.* **170** 265
[2] Faber T E 1972 *An Introduction to the Theory of Liquid Metals* (Cambridge: Cambridge University Press)
[3] Howson M A and Morgan G J 1985 *Phil. Mag.* **51**, 439
    Howson M A, Greig D, Gallagher B L and Morgan G J 1984 *J. Non-Cryst. Solids* **61&62** 1261
    Morgan G J and Weir G F 1984 *J. Non-Cryst. Solids* **61&62** 1319
[4] Harris R 1986 *J. Phys. F: Met. Phys.* **16** 53
[5] Busch G and Guntherodt H J 1974 *Solid State Phys.* **29** 335
[6] Movaghar B 1985 *Physics of Disordered Materials* ed D Adler, H Fritzsche and S R Ovshinsky (New York: Plenum) p 399
[7] Nguyen-Manh D, Mayou D, Morgan G J and Pasturel A 1987 *J. Phys. F: Met. Phys.* **17** 999
[8] Harris R and Houari A 1990 *Phys. Rev.* B **41** 5487
[9] Harris R and Houari A 1990 *Phys. Rev.* B **42** 7266
[10] Fraser D P, Zuckermann M J and Mouritsen O G 1990 *Phys. Rev.* A **42** 3186
[11] Berezin A A 1985 *Phys. Rev.* B **33** 2122
[12] See for example: Ballentine L E and Hammerberg J 1984 *Can. J. Phys.* **62** 692
[13] Krey U, Ostermeier H and Zweck J 1987 *Phys. Status. Solidi* B **144** 203
    Ostermeier H and Krey U unpublished
[14] Morgan G J and Howson M A 1985 *J. Phys. C: Solid State Phys.* **18** 4327
    Morgan G J, Howson M A and G F 1984 *J. Non-Cryst. Solids* **61&62** 1131
[15] Bhattacharya A K, Brauwers M, Brouers F and Joshi S K 1976 *Phys. Rev.* B **13** 5214; see also reference [13]
[16] As discussed in references [8] and [9], the participation ratio is defined in terms of the N coefficients a_{mi} of the tight-binding wavefunctions ψ_m as $\mathcal{R}_m = [\sum_i a_{mi}^2]^2/N \sum_i a_{mi}^4$. For highly disordered metals, we expect $\mathcal{R}_m \sim 1/3$.
[17] See discussion in reference [9]