Hall coefficient in pure metals: Lowest-order calculation for Nb and Cu

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The lowest-order solution to the linearized Boltzmann equation is calculated for Nb and Cu with uniform external electric and magnetic fields. This solution corresponds to a rigid displacement of the Fermi surface, and should be accurate when the anisotropy of the electron scattering function is small. For Cu the result agrees very well with experiment. The agreement with experiment for Nb is within 14%.

The Hall coefficient R_H has been measured in many metals.[1] Interpretation of the coefficient is more difficult for metals than for semiconductors because of the more complicated Fermi-surface topology. Relatively few calculations of the Hall coefficient have been made for transition metals.[2-5] A method for calculation R_H was given by Jones and Zener,[6] and more recently by Hasegawa and Kasuya[5] (HK). Jones and Zener assume no anisotropy of scattering; HK allow for anisotropy but find very little at room temperature for Cu. An expression for R_H equivalent to the theory of Ref. 6 was given by Tsuji[7]:

$$R_H = \frac{-1}{6e\hbar c} \frac{\sum_k v_k^3 (\overline{1/\rho})_k \left(\frac{-\partial f}{\partial \epsilon_k}\right)}{\left[\sum_k v_{kx}^2 \left(\frac{-\partial f}{\partial \epsilon_k}\right)\right]^2}, \tag{1}$$

where $(\overline{1/\rho})_k$ is the mean curvature of the Fermi surface at the point k. The notation k is short for $(\vec{k}\, n)$, the wave-vector and band index of an electron of energy ϵ_k and velocity $\hbar\vec{v}_k = \partial\epsilon_k/\partial\vec{k}$. The Fermi-occupation factor is denoted f. The interpretation of Eq. (1) is that R_H is a measure of curvature. For a free-electron sphere $(\overline{1/\rho})$ is $1/k_F$ and Eq. (1) yields $R_H = -1/nec$. For nonspherical surfaces, Eq. (1) can differ strongly from $-1/nec$ because regions with large v_k or large curvature are more heavily weighted. The Fermi surface of Cu, for example, is an electron surface by any reasonable definition, but the curvature $(\overline{1/\rho})_k$ is negative over significant regions near the necks. These happen to be regions of relatively low v_k so R_H is negative as expected, but in principle the result could have been positive if the v_k's had been different.

The evaluation of Eq. (1) is straightforward, provided one has values of $\vec{v}_k$ on a fine mesh of $\vec{k}$ points on the Fermi surface. In particular, it is not necessary to know components of $\vec{\nabla}_k v_{kx}$ normal to the Fermi surface as may be seen by writing R_H as

$$R_H = \frac{-1}{2e\hbar c} \frac{\sum_k v_{ky} (\vec{v}_k \times \vec{\nabla}_k v_{kx})_z \left(\frac{-\partial f}{\partial \epsilon_k}\right)}{\left[\sum_k v_{kx}^2 \left(\frac{-\partial f}{\partial \epsilon_k}\right)\right]^2}. \tag{2}$$

Equation (2) shows that only those components of $\vec{\nabla}_k v_{kx}$ normal to $\vec{v}_k$, that is only those components of $\vec{\nabla}_k v_{kx}$ lying on the Fermi surface, contribute to the sum. A derivation of Eqs. (1) and (2) is given in the Appendix. It is shown there that these equations follow from a very simple ansatz that the whole Fermi surface is displaced in a direction given by $\vec{E} + a(\vec{E} \times \vec{H})$, where a is a constant determined by the Boltzmann equation.

A Korringa-Kohn-Rostoker (KKR) program in the constant energy mode[8] was used to generate a mesh of $\vec{k}$ points on the Fermi surface. In the irreducible $\frac{1}{48}$ th, 492 points were used for Cu and 1060 points for Nb. In contrast, HK used 576 points over the Fermi surface of Cu which corresponds to 12 points in the irreducible $\frac{1}{48}$ th. The reason we used such a fine mesh was to reduce the error arising from computing the derivatives in Eq. (2) and in $(\overline{1/\rho})_k$ via the central difference technique.

Our calculated Hall coefficient for Cu is in excellent agreement with experiment. The agreement between our Nb calculation and experiment is approximately a 10% difference. In Table I, a summary of our results is presented. For Cu our value -5.30×10^{-11} m^3/C agrees well with Dugdale and Firth[2] and with the room-temperature value of Schmidt and Mann.[4] In the latter calculation an anisotropic scattering rate was used which gives rise to temperature variation of R_H at low T. The result of HK[5] is -6.25×10^{-11} m^3/C; the discrepancy probably derives from their coarser mesh.

The difference between our result for Nb and experiment is perhaps due to our neglecting the anistropy of the scattering matrix. Recent calculations,[9] using the rigid-muffin-tin approximation, of the rms anisotropy of $1/\tau$ at $T > \Theta_D$ yield 5%, 3%, and 2% for the Nb Γ, P, and N sheets, respectively, and 16% for Cu. The mean

TABLE I. Calculated parameters for Nb and Cu. The density of states $N(0)$ is in units of states per spin-rydberg-atom. The rms Fermi velocity is defined as $v_F=\left[\sum_k \delta(\epsilon_k) v_k^2 / \sum_k \delta(\epsilon_k)\right]^{1/2}$ and is in units of 10^8 cm/s. The mean curvature $\overline{(1/\rho)}_{av}$ is defined as $\sum_k v_k^3 (1/\rho)_k / N(0) v_F^3$ and is in units of 10^7 cm. Hall coefficients are in units of 10^{-11} m^3/C. Experimental values come from Refs. 2, 15, and 16. The symbols Γ, N, P for niobium refer to the three sheets of Fermi surface: the "jack" centered on $\vec{k}=0$ (Γ), the N-point ellipses (N), and the "jungle gym" (P).

	$N(0)$	v_F	$\overline{(1/\rho)}_{av}$	R_H^{theor}	R_H^{expt}
Cu	1.89	1.080	2.83	−5.30	−5.17
Nb Γ	1.51	0.142	−6.72		
Nb N	3.74	0.411	−46.98		
Nb P	4.69	0.541	3.16		
Nb_{tot}	9.94	0.553	−50.54	7.52	8.75

values of $1/\tau$ on different sheets in Nb differ by $\lesssim 8\%$.[10] Experiment[11] indicates that this may be an underestimate in Nb. We estimate an uncertainty of ~10% in R_H from anistropy effects. As the coefficients found using either Eq. (1) or (2) are within 3% of one another, numerical accuracy is not a problem.

A final source of discrepancy between theory and experiment lies in the fact that transport properties are sensitive to quasiparticle velocities $\vec{v}_k$. Our band structures agree well with Fermi-surface areas measured by techniques such as de Haas–van Alphen oscillations. Comparison of theoretical and experimental velocities is less well defined, partly because of mass-enhancement effects. In principle, a "quasiparticle" band structure rather than a local-density approximation to a "ground-state" band structure is needed for $\vec{v}_k$. The fact that our band structures for Nb and Cu give reasonable agreement with measured R_H is thus an interesting and gratifying result.

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APPENDIX

First we shall derive Eq. (2) and then show the equivalence of Eq. (2) and Eq. (1). The distribution function is written as

$$F_k = f_k + \phi_k\left(-\frac{\partial f}{\partial \epsilon_k}\right) \tag{A1}$$

which defines ϕ_k. The other symbols were defined in the text. The linearized Boltzmann equation is

$$\left(-e\,\vec{v}_k\cdot E + \frac{e}{\hbar c}\,\vec{H}\cdot(\vec{v}_k\times\vec{\nabla}_k\phi_k)\right)\left(\frac{-\partial f}{\partial \epsilon_k}\right) = \sum_{k'} Q_{kk'}\phi_{k'}, \tag{A2}$$

where the structure of the scattering operator $Q_{kk'}$, is immaterial for lowest-order Hall-coefficient calculations. We expand ϕ_k as

$$\phi_k = \phi_0 \vec{v}_k\cdot\vec{E} + \phi_1 \vec{v}_k\cdot(\vec{E}\times\vec{H}), \tag{A3}$$

where ϕ_0 and ϕ_1 are constants to be determined shortly. If we then let $\vec{E}=E\,\hat{x}$, $\vec{H}=H\hat{z}$ and insert Eq. (A3) into (A2) and equate powers of H, we have, through linear terms,

$$-e\,v_{kx}\left(\frac{-\partial f}{\partial \epsilon_k}\right) = \phi_0 \sum_{k'} Q_{kk'} v_{k'x}, \tag{A4}$$

$$-\frac{e}{\hbar c}\,\phi_0 (\vec{v}_k\times\vec{\nabla}_k v_{kx})_z\left(\frac{-\partial f}{\partial \epsilon_k}\right) = \phi_1 \sum_{k'} Q_{kk'} v_{k'y}. \tag{A5}$$

The coefficients ϕ_0 and ϕ_1 can then be determined and are written as

$$\phi_0 = -e \sum_k v_{kx}^2 \left(\frac{-\partial f}{\partial \epsilon_k}\right) \Big/ \sum_{kk'} Q_{kk'} v_{kx} v_{k'x}, \tag{A6}$$

$$\phi_1 = \frac{-e\,\phi_0 \sum_k v_{ky}(\vec{v}_k\times\vec{\nabla}_k v_{kx})_z \left(\frac{-\partial f}{\partial \epsilon_k}\right)}{\hbar c \sum_{kk'} Q_{kk'} v_{ky} v_{k'y}}. \tag{A7}$$

The current density is given by

$$\vec{j} = -2e \sum_k \vec{v}_k \phi_k \left(\frac{-\partial f}{\partial \epsilon_k}\right). \tag{A8}$$

Due to our choice of $\vec{E}$ and $\vec{H}$ the current in the z direction vanishes; the current in the other directions is written as

$$j_x = -2e\,\phi_0 \sum_k v_{kx}^2 \left(\frac{-\partial f}{\partial \epsilon_k}\right), \tag{A9}$$

$$j_y = -2e\,\phi_1 \sum_k v_{ky}^2 \left(\frac{-\partial f}{\partial \epsilon_k}\right). \tag{A10}$$

From Eqs. (A9) and (A10) we find the Hall coefficient to be given by Eq. (2). An alternate derivation of Eq. (2) using Chambers's method is given by Kittel.[12]

To show that Eqs. (1) and (2) are equivalent consider solely the numerator of Eq. (2), namely,

$$\sum_k v_{ky}(\vec{\nabla}_k \times \vec{\nabla}_k v_{kx})_z \left(\frac{-\partial f}{\partial \epsilon_k}\right). \tag{A11}$$

Expanding the cross product and using cubic symmetry we have

$$\frac{1}{\hbar^3}\sum_k \left[\left(\frac{\partial \epsilon}{\partial k_y}\right)^2 \frac{\partial^2 \epsilon}{\partial k_x^2} - \frac{\partial \epsilon}{\partial k_x}\frac{\partial \epsilon}{\partial k_y}\frac{\partial^2 \epsilon}{\partial k_x \partial k_y}\right]\left(\frac{-\partial f}{\partial \epsilon_k}\right). \tag{A12}$$

Tsuji[7] has shown that the quantity in the square brackets is equal to

$$\frac{1}{3}\left(\frac{\overline{1}}{\rho}\right)_k (|\vec{\nabla}_k \epsilon_k|)^3, \tag{A13}$$

from which Eq. (1) immediately follows. Alternatively one could use the fact that, for a surface given by $\epsilon(k_x, k_y, k_z) =$ constant,[13]

$$2\left(\frac{\overline{1}}{\rho}\right) = -\sum_{r=x,y,z} \frac{\partial}{\partial k_r}\left\{\frac{\partial \epsilon}{\partial k_r}\left[\sum_{s=x,y,z}\left(\frac{\partial \epsilon}{\partial k_s}\right)^2\right]^{-1/2}\right\}. \tag{A14}$$

Evaluating Eq. (A14), multiplying by $(\hbar v_k)^3/6$, and summing the result over k yields the numerator of Eq. (1). For our calculation of the curvature of the Fermi surface we used a different formula,[14] namely,

$$\left(\frac{\overline{1}}{\rho}\right) = \tfrac{1}{2}\sum_{\alpha,\beta} a^{\alpha\beta} b_{\alpha\beta} \quad (\alpha, \beta = 1, 2), \tag{A15}$$

$$a^{\alpha\beta} = a^{-1}_{\alpha\beta}, \tag{A16}$$

$$a_{\alpha\beta} = \frac{\partial \vec{k}}{\partial u^\alpha} \cdot \frac{\partial \vec{k}}{\partial u^\beta}, \tag{A17}$$

$$b_{\alpha\beta} = -\tfrac{1}{2}\left(\frac{\partial \vec{k}}{\partial u^\alpha} \cdot \frac{\partial \hat{n}}{\partial u^\beta} + \frac{\partial \vec{k}}{\partial u^\beta} \cdot \frac{\partial \hat{n}}{\partial u^\alpha}\right). \tag{A18}$$

Here $\hat{n}$ is the unit normal to the surface, i.e., $\vec{v}_k/|\vec{v}_k|$ and u^1, u^2 are two perpendicular directions along the surface.

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