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Hall coefficient of cubic metals

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A systematic study of the low-field Hall coefficient R_H of 23 cubic metals is done using tabulated Slater-Koster parameters for the band structure and a tetrahedron method to calculate the Fermi-surface integrals. In the approximation of an isotropic relaxation time, the Hall coefficient depends only on the Fermi-surface topology. The effect of the band structure is reflected in deviations of R_H from the free-electron values $-1/ne$. In favorable cases, our calculations agree to $\approx \pm 10\%$ with experimental data. Some of the deviations can be traced back to inaccurate band structures, e.g., in Cs or to rapidly changing R_H with ε_F leading to problems with convergence, e.g., in Pt. Discrepancies with experiment show the need for an anisotropic relaxation time, especially in Pd where small regions of high curvature dominate the Hall coefficient and in Al where two bands cross the Fermi surface. The similarity in the band structures of Rh, Pd, and Ag encourages the use of a rigid-band model, which agrees qualitatively with the experimental Hall coefficients for the alloys Rh-Pd and Pd-Ag.

I. INTRODUCTION

The transport properties of high-T_c superconductors, including Hall coefficients R_H, have been a rich source of confusion. Currently, it is being argued whether these data support a Fermi-liquid model. In light of this, it seems reasonable to examine carefully the metallic elements with conduction electrons of *s*, *p*, and *d* character which are described by the band Fermi-liquid picture. In particular, in this paper we examined how well the low-field Hall coefficient R_H is understood.

Hurd[1] has reviewed both theory and experiment for the Hall coefficient R_H; relatively few detailed calculations have been published. Beaulac, Pinski, and Allen[2] calculated the weak-field Hall coefficient of Cu and Nb with isotropic relaxation time. Beaulac and Allen[3] introduced an anisotropic relaxation time to explain the Hall coefficient of Pd. Hasegawa[4] and Leavens and Laubitz[5] used the variational solution of the Boltzmann equation to calculate the electrical conductivity and the relaxation time of K which was then used to compute the Hall coefficient. A nearly converged solution of the Boltzmann equation for Cu was done by Beaulac and Allen.[6] Butler[7] has used the coherent-potential approximation to calulate R_H in Pd-Ag alloys.

This paper is a systematic calculation of Hall coefficients for cubic metals, including the alkali metals, the noble metals, Al and Pb, some of the alkaline earth, and most of the transition metals. The Hall coefficient is calculated in the lowest order in the relaxation-time approximation, using a formula given by Tsuji.[8] In most cases we assume an isotropic relaxation time. Our band structures are tight-binding interpolations fitted by Papaconstantopoulos.[9] The results for most of the 23 cubic metals are in good agreement with experimental data. Deviations from experiment can be plausibly associated with either inaccurate band-structure representations, numerical problems associated with the band structure, or anisotropy of the relaxation time.

In the low-field limit the Hall coefficient R_H for cubic metals is given by

$$R_H = \sigma_H / \sigma_0^2 \,, \tag{1}$$

where σ_0 is the conductivity,

$$\sigma_0 = \frac{e^2}{3\hbar^2} \sum_{\mathbf{k}} \tau(k) [\nabla_{\mathbf{k}} \varepsilon(k)]^2 \left(\frac{-\partial f(\varepsilon)}{\partial \varepsilon} \right) , \tag{2}$$

σ_H the Hall conductivity,

$$\sigma_H = \frac{e^3}{6\hbar^4} \sum_{\mathbf{k}} \tau^2(k) \overline{\left[\frac{1}{\rho(k)} \right]} |\nabla_{\mathbf{k}} \varepsilon(k)|^3 \left(\frac{-\partial f(\varepsilon)}{\partial \varepsilon} \right) , \tag{3}$$

and k is an abbreviation for wave vector $\mathbf{k}$, band index n, and spin σ. The mean reciprocal curvature $\overline{1/\rho}$ at point k is expressed in terms of velocities $\mathbf{v}_k$ and the inverse mass tensor M^{-1} by

$$2 \overline{\left[\frac{1}{\rho(k)} \right]} |\nabla_{\mathbf{k}\varepsilon}(k)|^3 = \hbar^4 \mathbf{v}_k [\mathrm{Tr}(M^{-1}) - M^{-1}] \mathbf{v}_k \,, \tag{4}$$

where a particular element of M^{-1}, denoted by $(1/m)_{\alpha\beta} = (1/\hbar^2)\partial^2\varepsilon/\partial k_\alpha \partial k_\beta$.

The function $(-\partial f/\partial\varepsilon)$ is approximated by $\delta(\varepsilon - \varepsilon_F)$. For a detailed derivation see Ref. 1 and references therein.

Since the relaxation time appears to quadratic order in the Hall conductivity σ_H and to linear order in the conductivity σ_0, the Hall coefficient does not depend on the absolute strength of the relaxation time but only on the distribution of $\tau(k)$ on the Fermi surface (FS). If the relaxation time $\tau(k)$ is isotropic, the Hall coefficient R_H is indeed independent of τ.

For a spherical FS the expression for R_H reduces to the well-known formula for free electrons,

$$R_H^{\text{free}} = -1/ne \ , \tag{5}$$

where n is the electron density.

II. COMPUTATIONAL METHOD

We use Eqs. (1)–(3) to calculate the Hall coefficient in a variety of cubic metals using the parametrized tight-binding bands obtained by Papaconstantopoulos.[9] The underlying band-structure calculations do not include spin-orbit effects which may become important in the heavier metals.

The integrals over the Brillouin zone (BZ) are performed by using the linear tetrahedron method[10,11] with the correctly symmetrized weighting of **k** points.[12] The irreducible BZ is covered by a uniform mesh of up to 3281 (fcc) and 1785 (bcc) **k** points. The integration region is divided into cubes and tetrahedra that cover the entire irreducible BZ according to Ref. 13. Within a tetrahedron, the integral is approximated by linear interpolation. The accuracy of this scheme can be increased by using a finer mesh. Additional **k** points for this finer mesh are generated by quadratic interpolation.

The Fermi energies ε_F are found by integrating the density of states and are in good agreement with Ref. 9, with small improvements arising from a finer mesh and improved weighting.

Computation times on a SUN Sparc workstation range from several minutes for 85 and 55 **k** points in the irreducible BZ for fcc and bcc structures, respectively, up to about 3 h for 3281 **k** points.

III. RESULTS

Our results are summarized in Table I. When not stated otherwise, an isotropic relaxation time for all bands is assumed. The stated uncertainties in the calculated Hall coefficient were determined from the last two meshes after the calculation of R_H seemed to have converged. The free-electron values in Table I are calculated using the usual number of "free" electrons, i.e., one for the alkali metals, noble metals, and group-VB and -VIB metals; two for the alkaline-earth metals; three for Al and four electrons for Pb. For transition metals, no sensible "usual" choice exists; Table I assumes one electron per atom in these cases. The Hall coefficient is given in units of $10^{-11}\ \mathrm{m^3\,C^{-1}}$.

In some metals (e.g., Pd) it is appropriate to explore possible consequences of anisotropic relaxation times. The band structure provides the necessary information about the FS topology. The knowledge of FS velocity and curvature is helpful in designing an anisotropic $\tau(\mathbf{k})$. Since metals of the same group have similar Fermi surfaces the anisotropy model should lead to results closer to experiment for all elements of that group.

A. Alkali metals: Li, Na, K, Rb, and Cs

All alkali metals have a bcc structure and their FS is nearly spherical, i.e., with nearly constant mean curvature and velocity on the FS. Hence the Hall coefficient is expected to be close to the free-electron result given by $R_H^{\text{free}} = -1/ne$.

TABLE I. Hall coefficient for alkali metals, alkaline-earth metals, noble and NFE, group-VIII and group-VB and -VIB metals. The unit of R_H is $10^{-11}\ \mathrm{m^3C^{-1}}$. Experimental data are from Ref. 1, taken at room temperature.

Element	R_H^{free}	R_H^{calc}	R_H^{expt}
Li	-13.2	-12.8 ± 0.1	-15.0
Na	-24.5	-24.6 ± 0.1	-24.8
K	-44.6	-44.8 ± 0.1	-42.8
Rb	-54.7	-54.2 ± 0.1	-50.0 to -59.2
Cs	-68.6	-53.4 ± 0.2	-73.3
Ca	-54	-60 ± 10	-17.8
Sr	-70	?	?
Ba	-78	-110 ± 20	?
Cu	-7.3	-5.2 ± 0.2	-5.17
Ag	-10.4	-8.5 ± 0.2	-8.81
Au	-10.5	-8.1 ± 0.2	-7.16
Al	-3.4	-1.7 ± 0.3	-3.4 ± 0.5
Pb	-4.7	-2.4 ± 0.3	-0.9 ± 0.2
Rh	-7.5	11 ± 3	5.00
Ir	-8.8	5 ± 2	3.18
Pd	-9.1	-17 ± 3	-7.60 ± 0.2
Pt	-9.4	?	-2.30 ± 0.1
V	-8.6	7.3 ± 0.5	7.9 ± 0.3
Nb	-11.2	7.4 ± 0.5	8.7 ± 0.5
Ta	-11.2	7.4 ± 0.5	9.2 ± 1.0
Cr	-7.4	13.0 ± 2.0	36.0
Mo	-9.7	10.0 ± 2.0	18.0 ± 0.2
W	-9.8	$10.0\pm?$	11.5 ± 0.5

Our calculations are very close to both the free-electron result and experimental data as shown in Table I. Only for Cs our calculated Hall coefficient disagrees considerably with experiment. A closer look into the band structure produced from the Slater-Koster (SK) parameters shows that it produces a neck in the $\langle 110\rangle$ direction for Cs which is not seen in de Haas–van Alphen measurements.[14] The necks are therefore a spurious effect of either the underlying augmented plane-wave energy bands, or, more likely, the SK interpolation which is not ideally suited for nearly-free-electron (NFE) metals. The discrepancy between our calculated and measured Hall coefficients for Cs occurs because there is no FS point along ΓN since the N point has an energy lower than ε_F. Reducing the Fermi energy ε_F by ~ 7 mRy yields a closed FS and the Hall coefficient changes by about 40% to give a value very close to the experimental result. An anisotropic relaxation time $\tau(\mathbf{k})$ has only a small effect on the Hall coefficient. For example, in potassium, a model where $\tau=\tau_1$ in a cone with opening angle $2\alpha=20°$ along a $\langle 110\rangle$ direction, $\tau=\tau_0$ elsewhere, yielded a change of less than 10% in R_H when $\tau_1/\tau_0=0.7$.

B. Noble metals: Cu, Ag, and Au

Noble metals, especially Cu, are some of the most studied metals of all. They crystallize in the fcc structure. Their FS is well known and consists of a belly and a neck in the $\langle 111 \rangle$ direction. The free-electron results are larger by about 30% than experiment. Our results, on the other hand, are within 5% of the experimental data for Cu and Ag and within 15% for Au. The reduction in the Hall coefficient from the free-electron results is caused by the contribution from the neck regions where the curvature has the opposite sign from that of the belly region.

One of the earliest studies of relaxation-time anisotropy $\tau(\mathbf{k})$ was done on Cu.[15] To investigate the influence of anisotropy of τ on R_H we use a model of relaxation time given by $\tau=\tau_1$ in the neck region (within ±10° of the $\langle 111 \rangle$ direction) and $\tau=\tau_0$ elsewhere. R_H changes from the isotropic value -5.2 to -4.7 for $\tau_1/\tau_0=0.7$ and to -4.9 for $\tau_0/\tau_1=0.7$. Another model used by Beaulac and Allen,[3] which is motivated by the FS geometry of Pd, is given by $\tau=\tau_1$ within ±6° of the ΓXL plane and $\tau=\tau_0$ elsewhere. For the same ratios of the relaxation times, i.e., for $\tau_1/\tau_0=0.7$ the Hall coefficient changes from the isotropic value -5.2 to -4.5 and for $\tau_0/\tau_1=0.7$ it changes from -5.2 to -5.6. The effects on Ag and Au are similar. This shows that the relaxation-time anisotropy has only a small effect on R_H of noble metals.

C. Nearly-free-electron metals: Al and Pb

Aluminum and lead have an fcc structure and are examples of NFE metals. The free-electron value for the Hall coefficient for Al agrees well with experiment. However, as we discuss below this agreement is highly accidental and involves cancellations from regions of high curvature with opposite sign. With an isotropic relaxation time our calculation for Al yields only half the experimental result. The free-electron Hall coefficient for Pb is about five times larger than the experimental result, whereas the band-structure calculation brings it within a factor of 2.5.

Both Al and Pb have two bands (bands 2 and 3) at ε_F with curvatures $|\rho_2|$, $|\rho_3|$ in the ratio 2:1, ρ_2 is negative and ρ_3 positive. The conductivity σ_0 of Al is dominated by band 2 (6:1); in Pb they are comparable. Hence a modest ratio of the relaxation time in a two-band model can account for the deviation from experiment. In Al a ratio of the relaxation time in bands 2 and 3 of 0.8:1 and in Pb a ratio of 0.92:1 gives good agreement with data.

Another approach is to assign different scattering times to s, p, and d states yielding a weighted average of the form

$$\frac{1}{\tau(\mathbf{k})}=\sum_{l=0}^{2}\frac{w_l(\mathbf{k})}{\tau_l}\ , \tag{6}$$

where $w_l=|\langle l|\mathbf{k}\rangle|^2$ is the fractional tight-binding character of state $\mathbf{k}$ in angular momentum l satisfying $\sum_{l=0}^{2}w_l=1$. In Al, s and p states dominate up to ε_F and a ratio of $\tau_s:\tau_p:\tau_d\approx 1.6:1.0:1.0$ reproduces the experimental result. Applying the above model and the same ratios of the relaxation times to Pb leads to an improved Hall coefficient $R_H=-1.2$. This is surprising since the sates at the FS have only 10% s character on average, and yet the effect of introducing anisotropy between s and p states reduces the isotropic Hall coefficient by a factor of 2. In Al, on the other hand, the s character is about 40% and the anisotropic-relaxation-time model increases R_H by a factor of 2. Our calculated Hall coefficient, however, is in good agreement with experimental data at low temperatures.[1] This indicates that scattering in this temperature range is isotropic.

As an alternative (and equally satisfactory) model for Al, Böning *et al.*[16] found that the largest part of the FS has a low positive curvature as expected for an NFE metal, but near the K and U symmetry points the FS has two small regions with large curvatures of opposite signs. They suggested that by an appropriate choice of relaxation times, these two high-curvature regions could cancel each other, thereby recovering the free-electron result.

The extreme sensitivity of the theoretical R_H of Al to anisotropy of τ is confirmed by experimental observation of extreme sensitivity to impurities, radiation damage, and temperature.[16] In the presence of these perturbations the Hall coefficient tends to increase, sometimes even yielding a positive sign. This can be interpreted as a change in the anisotropy of τ, whereas changes of the FS play a minor role. These results would be very hard to understand if a free-electron picture were applied.

This discussion shows very clearly that the approximation of Al and Pb as NFE metals is valid only in a limited sense. Certain quantities, e.g., the velocity on the FS, are close to the free-electron result. However, the Hall coefficient, which depends also on the curvature of the FS, deviates from free-electron behavior.

D. Group VIII: Rh, Ir, Pd, and Pt

These four fcc metals show some of the difficulties that may be encountered in calculating the Hall coefficient. Their FS consist of two (Pt), three (Pd,Ir), or even four (Rh) sheets which make an analysis of the Hall coefficient much more difficult than in the previous cases where the FS had only one or two sheets. The case of Pd has been studied before[3] and is easy insofar as the overwhelming contribution to the Hall coefficient comes from the Γ-centered sheet. The disagreement between the theoretical result and experimental data can be corrected by a simple anisotropic τ within ±6° of the ΓXL plane. A ratio of $\tau_1/\tau_0\sim 0.7$ is sufficient to account for the discrepancy. Applying this model of relaxation time to Rh also yields the experimental value of the Hall coefficient.

The Hall coefficient of Pt failed to yield the correct sign. The difficulty here is that very close to the Fermi energy (within 10 mRy) the Hall coefficient changes sign abruptly. Bands 5 and 6 have very large curvatures but of opposite sign in the ΓXL plane; band 5 dominates up to ε_F and band 6 is important above it. The calculated Hall coefficient is therefore very sensitive to slight corrections of the band structure around ε_F and to anisotropy in the relaxation time; the results of a fully converged (but isotropic scattering) calculation would thus not be very meaningful. A calculation of the Hall coefficient for Pt by Dosdale and Livesey[17] found that the conductivity σ_0 and the Hall coefficient showed a two-peaked structure as a function of velocity. By assigning a relaxation time ratio of 0.73 for fast over slow electrons they were able to reproduce the experimental result.

E. Group-VB and -VIB metals: V, Nb, Ta; Cr, Mo, and W

These six metals crystalize in the bcc structure. The group-VB metals have two bands and the group-VIB metals have three bands cutting the Fermi energy ε_F. Our results are close to the experimental results except for Mo and Cr. In the case of Cr this is not surprising since in our calculations Cr is treated as a normal bcc metal and we do not include the fact that Cr is an antiferromagnet with a Néel temperature of 321 K. The free-electron model in all cases already fails in predicting the right sign for the Hall coefficient.

F. Alkaline-earth metals: Ca, Sr, and Ba

Experimental data are only available for Ca which disagree with our result. The band structure of Sr yields a semimetal with practically zero density of states (DOS) at ε_F. The computation of the Hall coefficient is difficult since it does not converge in this "gap" region. Our result for Ba could be considered a prediction, but we do not have especially high confidence in our number at this stage.

IV. HALL COEFFICIENT IN ALLOYS

We discuss the use of a simple rigid-band model to obtain the Hall coefficient in alloys of Rh, Pd, and Ag which have similar band structures. We expect the Hall coefficient as a function of energy to show the same qualitative behavior for all three metals. In Fig. 1 we show the band structure of Pd with the relative positions of the Fermi levels of these three metals. The d bands span a range of about 0.4 Ry. The Fermi levels of Rh and Pd lie in these d bands. The Fermi level of Ag which has one additional electron is higher since the density of states above the d bands is lower than in the d bands.

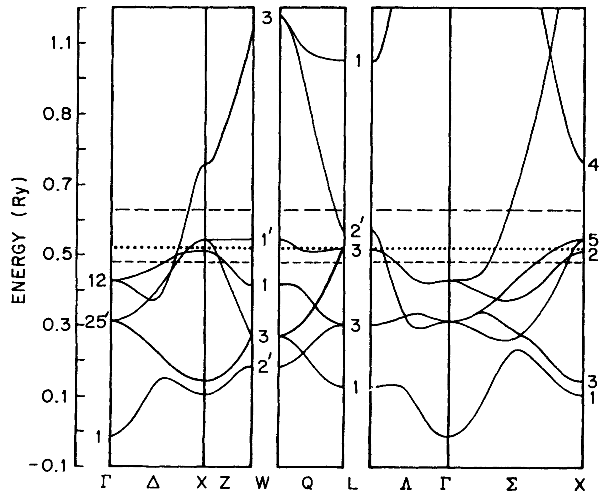

FIG. 1. Band structure of Pd. The dotted line indicates the Fermi energy of Pd. The relative positions of the Fermi energies of Ag (upper dashed line) and Rh (lower dashed line) are shown. Taken from Ref. 9.

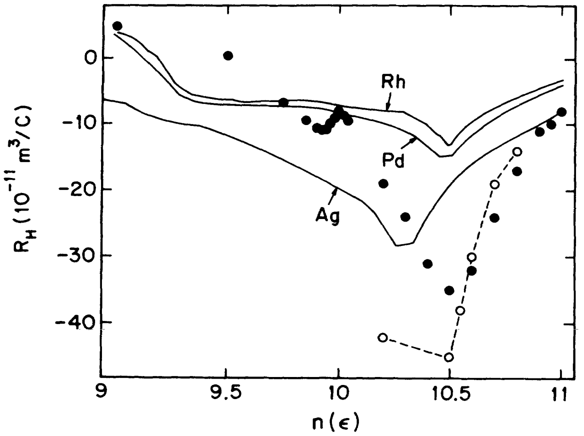

FIG. 2. Hall coefficient R_H vs the number of electrons $n(\varepsilon)$ from rigid-band models based on Rh, Pd, and Ag. The solid lines are our calculations, the solid circles are the experimental data of the alloys Rh-Pd and Pd-Ag from Refs. 18 and 19, and the open circles are calculated values (at room temperature) from Ref. 7.

In Fig. 2 we show the rigid-band model Hall coefficient calculated as function of the number of electrons $n(\varepsilon)$ obtained by integrating the DOS. For example, $n(\varepsilon)=9$ corresponds to pure Rh, $n(\varepsilon)=10$ to pure Pd, and in between it corresponds to the alloy Rh-Pd. We assume that the Hall coefficient of Rh-Pd (similarly for Pd-Ag) can be obtained at least qualitatively by putting more electrons into Rh or by taking up to one electron out of Pd. Anisotropy was included using the model of Eq. (6). Figure 2 shows that experimental values[18,19] of R_H for the alloys exhibit trends which are qualitatively contained in the rigid-band model. Quantitative agreement is not as good as with the coherent-potential approximation calculations of Butler[7] which are also shown. The sharp cusp near $n=10.5$ and the sign change near $n=9.5$ are both qualitatively contained in our results. The sharp feature at $n=10$ is probably a result of change in scattering anisotropy as pure Pd is altered by alloying.[20]

V. DISCUSSION

The results of our study show that R_H even in elemental metals is a fairly complicated quantity, but can be accounted for in a Fermi-liquid model provided band-structure effects are included. We verified that modest anisotropy of $\tau(\mathbf{k})$ has little effect on R_H in alkali and noble metals, but for Pd and related metals the effect is bigger, as it is in Pb. In Al the effect is dramatic, because of accidental near cancellations. As one can see from Eqs. (1)–(3) we only need the relative anisotropies in order to be in better agreement with experimental results.

Since we do not know the absolute value of the relaxation time we cannot easily compare the Hall coefficient results with other transport data. The variational principle for the conductivity implies that modest anisotropies of the relaxation time change the conductivity only very little.

In high-T_c superconductors there is some evidence for a systematic large temperature dependence of R_H, approximately $1/T$ in form. Such behavior is not commonly found in the elements, but is not prohibited by the theory, and is in fact seen in some of the Pd-Ag alloys. Here the effect is probably explainable as a consequence of the T dependence inherent in $\tau(\mathbf{k})$ anisotropy. At low T, only alloy disorder scattering occurs with anisotropy of its own. Butler's calculation[7] includes this effect, which our calculation omits. As T increases, phonon scattering (with a different anisotropy) becomes increasingly important. It is hard to see how such a description could account for the systematic behavior of several different copper oxide systems.

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$$N_{\mathrm{fcc}}(n)=(n+2)(n^2+n+6[n/2]+6)/12\ ,$$

$$N_{\mathrm{bcc}}(n)=(n+2)(n^2+3n+6[n/2]+8)/24\ ,$$

where $n+1$ is the number of $\mathbf{k}$ points along ΓX or ΓH, respectively, and $[x]$ the Gauss symbol, denoting the largest integer less than or equal to x.

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