

## ***Ab Initio* Calculation of the Hall Conductivity: Positive Hall Coefficient of Liquid Fe**

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A first-principle calculation of the Hall coefficient of liquid Fe is performed by using the formula found by Itoh and the tight-binding, linear muffin-tin orbital, particle source method. The calculated coefficient is positive and agrees well with the experiment. Only ordinary potential scattering is involved in the calculation, and the positive Hall coefficient is thus explained without recourse to any special mechanism. It is also shown that the hybridization between  $p$  and  $d$  states plays an important role. [S0031-9007(98)07480-8]

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Since its first discovery on liquid Fe and Co [1], the occurrence of the positive Hall coefficient in disordered metals has been an outstanding problem for many years. There have been found by now a variety of materials which show the positive sign of the Hall coefficient in their liquid and amorphous states [2], and a common feature of these systems is that they all include the transition or the rare-earth metals as constituent elements.

In a recent article, the present authors investigated a single  $s$ -band tight-binding model [3], and claimed that the positive Hall coefficient can result from ordinary potential scattering, if we properly take into account the diamagnetic current. As a continuation of the work, we present in this Letter our preliminary calculations on liquid  $3d$  transition metals, and report that a quantitatively correct value of the coefficient is obtained for liquid Fe.

For the case of dc conductivities, it is already shown that the  $d$  states have a dominant contribution to the conduction [4]. These states hybridize with  $p$  states, and modify their electronic structure, particularly around the Fermi level. In the present calculation, we found that this change in the electronic structure due to the hybridization is essential to the sign reversal of the Hall coefficient in the liquid Fe. The conclusion is derived from a realistic *ab initio* calculation, and we hope to terminate the long controversy on this problem.

Our calculation is based on two elements. The first is the expression for the Hall conductivity derived by Itoh [5], which has been used in our earlier work [3] and which includes full contributions from the diamagnetic current. The formula is exact and tractable, particularly suitable for calculations using the Green functions. The second element is a scheme developed recently by Tanaka to calculate electronic transport properties from first principles [6]. It is a combination of the tight-binding linear muffin-tin orbital (TB LMTO) method [7,8] with the particle source method (PSM) [9], which, in fact, allows for the evaluation of any physical quantity described in terms of a product between the Green functions and other quantum operators. The formalism has already been applied

successfully to calculate the dc conductivity of liquid  $3d$  transition metals [6], and its extension to the Hall conductivity is also possible as explained below.

Itoh's expression [5] for the Hall conductivity represents the exact field-linear part of the off-diagonal element of the conductivity tensor. It is given in the form

$$\begin{aligned} \sigma_{xy}/B = & -\frac{\pi e^3 \hbar^2}{c} \int \frac{dE}{2\pi} \left( -\frac{\partial f}{\partial E} \right) \\ & \times \text{Im} \langle \text{Tr} [v_x G(E + i\eta) v_y \delta(E - H) \\ & \quad \times v_x G(E + i\eta) v_y \delta(E - H)] \rangle, \quad (1) \end{aligned}$$

where  $H$  and  $v$  are the one-electron Hamiltonian and the velocity operator. It has been derived directly from the Kubo formula for noninteracting electrons, and is therefore valid for any one-electron Hamiltonian. The above formula has two striking features of practical importance. First, the Hall conductivity is solely determined by the states on the Fermi surface. Second, the Green functions and the velocity operators involved in the preceding expression are those for the system *in the absence of a magnetic field*. Therefore, by using the above formula, the technical difficulty in the numerical evaluation of the Hall conductivity can be reduced to the level of the dc conductivity calculation, for which TB-LMTO PSM has been found very useful [6].

Let us outline the procedure of the calculation. In the TB-LMTO method, we first transform the Hamiltonian into a tight-binding representation in terms of localized and mutually orthogonal muffin-tin orbitals [7,8]. To be more precise, the transformed Hamiltonian is described, within atomic sphere approximation, as [7]

$$H = E_\nu + \bar{h} - \bar{h} \bar{\sigma} \bar{h} + \dots, \quad (2)$$

$$\bar{h}_{RL,R'L} = \bar{\omega}_{RI}(-) \delta_{RR'} \delta_{LL'} + \bar{\Delta}_{RI}^{1/2} \bar{S}_{RL,R'L} \bar{\Delta}_{R'I'}^{1/2}, \quad (3)$$

where  $R$  denotes the atomic site and  $L$  the set of azimuth and magnetic quantum numbers  $l$  and  $m$ . The parameter  $\bar{\sigma}$  defines a set of basis functions within each atomic sphere. The matrix element  $\bar{S}_{RL,R'L}$  is the screened structure constant, which depends only on the

atomic structure. The functions  $\bar{\omega}_{Rl}(-)$  and  $\bar{\Delta}_{Rl}^{1/2}$  are the potential parameters that should be determined self-consistently. The former gives the relative position of the band center, while the latter determines the bandwidth.

Once the Hamiltonian is given in the tight-binding form, we can immediately apply the PSM to evaluate the matrix elements of the Green functions [9]. This is performed by solving the time-dependent Schrödinger equation

$$i \frac{d}{dt} |\tilde{j}; t\rangle = H |\tilde{j}; t\rangle + |j\rangle \theta(t) e^{-i(E+i\eta)t} \quad (4)$$

for the state vector  $|\tilde{j}; t\rangle$ , on the initial condition  $|\tilde{j}; t=0\rangle = 0$ . Here  $|j\rangle$  is an arbitrary state vector,  $\eta$  is a finite small value, and  $\theta(t)$  is the step function. After a sufficiently long time  $T$ , the solution can be approximated as

$$|\tilde{j}; T\rangle \approx G(E + i\eta) |j\rangle e^{-i(E+i\eta)T}, \quad (5)$$

so that we can derive a state vector  $G(E + i\eta) |j\rangle$  from the solution by

$$G(E + i\eta) |j\rangle = \lim_{T \rightarrow \infty} |\tilde{j}; T\rangle e^{i(E+i\eta)T}. \quad (6)$$

If we take a basis vector for  $|j\rangle$ , then the preceding state vector consists of the matrix elements of the Green function operator. The relative accuracy of the preceding evaluation is determined by the evolution time  $T$  as  $\delta = e^{-\eta T}$ .

Since the preceding argument applies to any state vector  $|j\rangle$  chosen initially, we can extend the procedure to evaluate the matrix elements of a product including an arbitrary number of Green functions and/or other quantum operators. For example, the matrix elements of  $G(E + i\eta) A G(E + i\eta)$  can be evaluated by first obtaining the state vector  $G(E + i\eta) |j\rangle$  as mentioned previously, and then by replacing  $|j\rangle$  by  $A G(E + i\eta) |j\rangle$  in Eq. (4), namely, by repeating the same procedure twice.

We have calculated the Hall conductivity of liquid Fe, together with its electronic density of states and the dc conductivity, as outlined above. Before describing the results, we make a few comments on our actual calculations. The first is on the trace operation required in the calculation of each quantity. This is most conveniently done by introducing a random linear combination of the basis vectors

$$|\Phi\rangle = \sum_{n=1}^N |n\rangle e^{i\theta_n}, \quad (7)$$

with  $\{\theta_n\}$  being a set of independent random variables ranging from 0 to  $2\pi$ . By making use of a trivial property  $\langle e^{i\theta_n} e^{-i\theta_{n'}} \rangle_{\text{st}} = \delta_{nn'}$ , where  $\langle \rangle_{\text{st}}$  implies statistical average, the diagonal element of an arbitrary operator  $C$  with respect to  $|\Phi\rangle$  can be substituted for its trace,

$$\begin{aligned} \langle \Phi | C | \Phi \rangle &= \sum_n \langle n | C | n \rangle + \sum_{n \neq n'} e^{i(\theta_n - \theta_{n'})} \langle n | C | n' \rangle \\ &\approx \sum_n \langle n | C | n \rangle. \end{aligned} \quad (8)$$

The second term can be made very small by taking a statistical average over several different choices of the random

set  $\{\theta_n\}$ . In practice, we can even avoid this procedure if the amplitudes of the off-diagonal elements are densely and rather uniformly distributed, and if the number of basis vectors  $N$  is sufficiently large (the statistical error estimated to be proportional to  $1/\sqrt{N}$ ).

The second is on the form of the current operator, for which some ambiguity exists in the tight-binding calculation. In our calculation we have employed the following form:

$$(v_x)_{\alpha\beta} = \frac{i}{\hbar} H_{\alpha\beta} (x_\beta - x_\alpha), \quad (9)$$

where  $\alpha$  and  $\beta$  are orbital indices and  $x_\alpha$  denotes the  $x$  coordinate of the atomic site, on which the orbital  $\alpha$  is centered. The preceding expression is most commonly used in the tight-binding calculations. It neglects the off-diagonal elements of the position operator with respect to the basis orbitals, but they are usually small when the orbitals are localized. In the present calculation, we employed a model atomic structure consisting of 938 atoms, which was constructed by Satoh [10] by employing a semiempirical molecular dynamics method [11]. For the calculation of electronic structure, we have neglected the last term of the Hamiltonian (2), although it is not difficult to include it. This approximation is consistent with the assumption that the basis orbitals are mutually orthogonal. The self-consistency of the calculation has been achieved to keep up with the accuracy of the potential parameters averaged over constituent atoms.

Figure 1 shows the calculated dc and Hall conductivities, as functions of energy resolution  $\eta$ , which is included in the Schrödinger equation (4). As is seen from the figure, both conductivities have stable values for all values of  $\eta$ , and the Hall conductivity always shows a positive sign. A value of  $\eta$  represents the width of the imaginary part of the Green function, which turns into a real delta function in the limit of  $\eta \rightarrow 0$ . As  $\eta$  decreases from  $\eta = 0.20$ , both quantities increase monotonically at first, but the dc conductivity starts to decrease abruptly below  $\eta = 0.01$ . The Hall conductivity also follows a

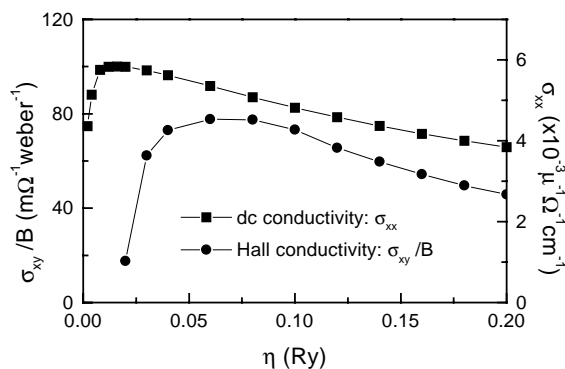


FIG. 1. Calculated dc and Hall conductivities of liquid Fe as functions of energy resolution  $\eta$ .

similar process of decrease, which starts at larger values of  $\eta$ , around  $\eta = 0.06$ .

The decrease of the calculated conductivities with decreasing  $\eta$  comes from the discrete nature of the energy levels of a finite system. According to the Kubo formula, successive transitions must take place in the vicinity of the Fermi level. The transition is possible only between those states in the width of  $\eta$  around the Fermi level. Therefore, in a finite system with discrete levels, the energy resolution should not be taken too small. In the present case, the critical value of  $\eta$  for a reliable calculation of the macroscopic dc conductivity is estimated to be around  $\eta = 0.01$ , for which the number of the *pairs of states* within the energy resolution becomes comparable to the number of atoms. Practically the same order of resolution is adopted in earlier conductivity calculations for a similar system size [4]. The condition is more severe for the Hall conductivity, because it is expressed in terms of *four* Green functions, instead of two in the case of the dc conductivity. It is therefore a nontrivial task to find the most reliable values of both conductivities.

In a recent calculation by Tanaka [6], it has been found that the diffusion constant (the ratio of the dc conductivity to the density of states) is remarkably insensitive to the value of  $\eta$  for  $\eta \geq 0.01$ , although the conductivity itself varies gradually with  $\eta$ . It has made possible a reliable extrapolation to small  $\eta$ , and the obtained value of the conductivity of amorphous Fe is very close to the experimental value. Here we have attempted a similar plot of the weak-field Hall coefficient

$$R_H = \frac{\sigma_{xy}/B}{\sigma_{xx}^2} \quad (10)$$

against  $\eta$  in Fig. 2. It has turned out that the Hall constant is also insensitive to  $\eta$ . As is seen from the figure, it stays almost constant throughout the resolution range of  $\eta > 0.1$ . We therefore identify this constant value to be the macroscopic Hall constant, which is evaluated to be  $R_H = 32.0 \times 10^{-11} \text{ (m}^3 \text{ A}^{-1} \text{ s}^{-1}\text{)}$ . The value agrees quantitatively with the experiment [1]. The positive Hall coefficient can thus be obtained from a one-electron Hamiltonian with only ordinary potential scattering, without recourse to other mechanisms such as skew scattering or scattering due to magnetic disorder. Compared to the previous calculations, however, a new ingredient is included. This is the diamagnetic current, as emphasized earlier [3,5], and we conclude that the diamagnetic current accounts for the positive Hall coefficient of liquid Fe.

We have also repeated the same calculations, with *s-p*, *p-d*, and *s-d* transfer integrals set equal to zero, in order to investigate the effect of hybridizations. Then the respective contribution from each orbital to the Hall conductivity was found to have a negative sign. By introducing three different hybridizations one by one, we found that the *p-d* hybridization is responsible for the

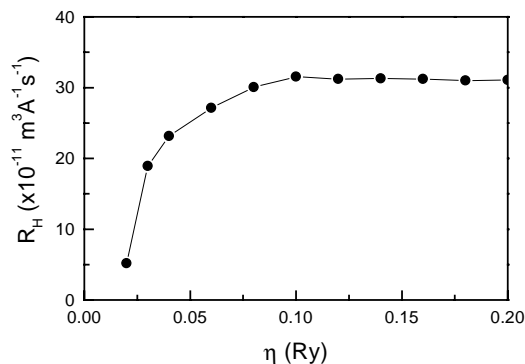


FIG. 2. Hall coefficient of liquid Fe as a function of energy resolution  $\eta$ .

sign reversal. This is shown in Fig. 3. As is clearly seen from the figure, the *p-d* hybridization not only turns the Hall conductivity positive, but also reduces its magnitude approximately by the factor of 3. The *p-d* hybridization has thus the greatest influence on the nature of the Hall conduction.

The effect of *p-d* hybridization on the electronic structure has also been examined in the same manner. Figure 4 compares two projected densities of states (DOS), with and without *p-d* hybridization. Without *p-d* hybridization, the projected density of *p* states resembles a simple-metal DOS. A drastic change is seen to occur in the projected density of *p* states when the *p-d* hybridization is introduced. The *p* states tend to separate into bonding and antibonding states, and a shallow dip is created in between. The Fermi level lies near the bottom of the dip. In our earlier study of a model disordered metal with a single *s*-band [3], we have shown that the sign reversal occurs for higher filling fractions of the band, and therefore claimed that the concept of a hole is not limited to Bloch electrons. If we apply the same scenario to the present case, a possible interpretation will be that “holes” created in the bonding *p* band dominate the Hall conduction, and become responsible for the positive contributions. From this viewpoint, there should be little difference between

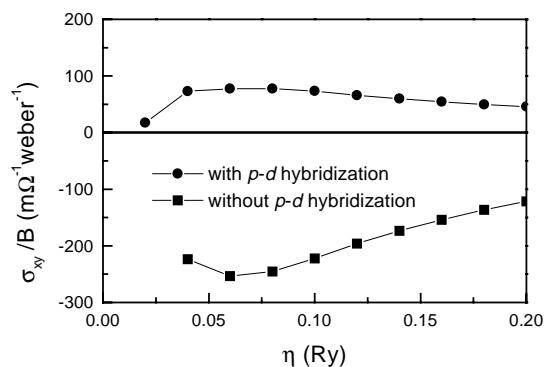


FIG. 3. Calculated Hall conductivities with and without *p-d* hybridization.

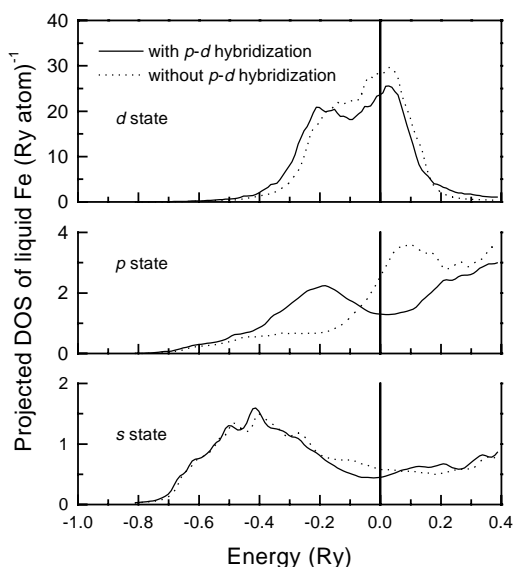


FIG. 4. Comparison of the projected DOS of liquid Fe with and without  $p$ - $d$  hybridization.

the disordered and the crystalline states. Indeed, many  $3d$  transition metals (V, Cr, Fe, and Co) show positive Hall coefficients in their crystalline states, and we may apply the same interpretation to these cases.

In summary, we have calculated the Hall conductivity of liquid Fe from first principles, including the diamagnetic current. The TB-LMTO PSM is employed, and the calculated Hall coefficient is positive and agrees well with the experimental value. It is shown that the positive Hall coefficient of liquid Fe can be explained by scattering

due only to structural disorder, and that the sign reversal originates from the diamagnetic current, through the interference between  $p$  and  $d$  waves in the course of their propagations, and the associated changes in the electronic structure.

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