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## CALCULATIONS OF ELECTRICAL TRANSPORT PROPERTIES OF LIQUID METALS AT HIGH PRESSURES

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It is shown how the usual nearly-free-electron model for the electrical resistivity of simple liquid metals can be extended to the case of liquid transition metals such as iron. A simple prescription is given for calculating the resistivity at different densities and temperatures. As an application and example of the method, calculations on liquid iron at different densities have

been carried out and the resistivity of molten iron in the Earth's outer core is estimated. The effects of alloying iron with other elements are also considered. The calculated conductivity of the outer core is well within the limit required for the dynamo model of the geomagnetic field and agrees well with some recent shock wave data.

### 1. Introduction

Over the last few years there has been considerable progress in understanding the electrical transport properties of liquid metals. A simple model for calculating the electrical resistivity and thermoelectric power was proposed by ZIMAN (1961). In this model the current in the liquid metal is carried by the "valence" or conduction electrons which are scattered by the disordered array of the ions or atoms. This scattering gives rise to the resistivity which can be calculated using a Boltzmann equation approach. Many calculations of the resistivity of "simple" liquid metals at normal pressures and temperatures have been carried out; see, for example, ASHCROFT and LEKNER (1966), FABER (1969) and EVANS (1970, 1971). The results of these calculations indicate that this simple nearly-free-electron (NFE) theory is capable of giving a good description of the magnitude of the resistivity, its temperature dependence and its behaviour on alloying. DICKEY *et al.* (1967) have calculated the resistivity of the liquid alkali metals at high pressures.

In the "simple" metals, i.e. those which are not noble or transition metals, the scattering properties of a single ion can be described using the pseudo or model potential technique. The basic idea behind this method is that of replacing the actual strong potential of the ion

by a weak potential in such a way that the ion retains the original *scattering* properties. This weak potential (the pseudo-potential) can then be used in the Born approximation in perturbative calculations of electronic properties HARRISON (1966).

In this paper, we indicate how the NFE model can be applied to non-simple metals and in particular to the transition metal iron where the pseudo-potential treatment is no longer valid. When iron atoms are brought together to form a metal, the atomic 3d levels are not completely destroyed but become virtual or resonant levels of the ionic potential (ZIMAN, 1971). This means that conduction electrons near the Fermi energy in iron are very strongly scattered by this potential. The energy at which the electron-ion scattering cross section is a maximum corresponds to the middle of the d band in metallic iron.

We calculate the resistivity of liquid iron at atmospheric pressure and close to its melting point and then evaluate the resistivity as a function of density with the aim of estimating the electrical conductivity  $\sigma$  of the Earth's outer core. The latter quantity is an important parameter in the dynamo model for the geomagnetic field. Several empirical values for  $\sigma$  have been proposed, most of them based on dubious extrapolations of known experimental data of one kind or another. We compare our calculated value of  $\sigma$  with some recent high-pressure shock-wave data and discuss effects of alloying iron with nickel and silicon.

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A preliminary account of the iron calculation was given by JAIN and EVANS (1972).

## 2. Outline of the theory

A derivation of the present model has been given by EVANS *et al.* (1971) and DREIRACH *et al.* (1972). The resistivity  $\rho$  can be written as:

$$\rho = \frac{3\pi\Omega_0}{e^2\hbar V_F^2} \int_0^1 4(q/2K_F)^3 a(q) |t(q/2K_F)|^2 d(q/2K_F), \quad (1)$$

where  $\Omega_0$  is the atomic volume of the liquid,  $V_F$  is the velocity of an electron at the Fermi energy,  $e$  is the electronic charge and  $q$  is a measure of the scattering angle for an electron on the Fermi sphere of radius  $K_F$ . The factor  $(q/2K_F)^3$  arises from the usual momentum transfer factor  $1 - \cos \theta$  in the Boltzmann equation result for the relaxation time. The distribution of the scatterers enters through  $a(q)$ , the liquid structure factor or interference function,

$$a(q) = N^{-1} \left| \sum_i \exp(iq \cdot \mathbf{R}_i) \right|^2, \quad (2)$$

where  $N$  is the number of ions and the average is over all ion sites  $\mathbf{R}_i$  in the liquid. This quantity can be measured directly in neutron or X-ray scattering experiments.

The scattering properties of a single site are introduced through the transition matrix  $t(\mathbf{K}, \mathbf{K}')$  which gives the probability of an electron in a plane wave state  $|\mathbf{K}\rangle$  being scattered into another state  $|\mathbf{K}'\rangle$  of the same energy by a single scattering event. If the potential at any scattering centre is spherically symmetrical, then we can write

$$t(\mathbf{K}, \mathbf{K}') = \frac{-2\pi\hbar^3}{\Omega_0 m (2mE)^{\frac{1}{2}}} \times \sum_l (2l+1) \sin \eta_l(E) \exp(i\eta_l(E)) P_l(\cos \theta), \quad (3)$$

where  $\eta_l$  are the angular momentum phase shifts of this potential. Now  $t$  has the dimensions of energy and is normalised to the atomic volume,  $q = |\mathbf{K} - \mathbf{K}'|$ , and  $\theta$  is the angle between  $\mathbf{K}$  and  $\mathbf{K}'$ .  $P_l(\cos \theta)$  is the usual Legendre polynomial. The phase shifts are evaluated at the Fermi energy  $E = E_F$  measured relative to the zero of energy  $E_{MTZ}$  in the liquid metal;  $m$  is the electron mass.

In transition metals, the d phase shift  $\eta_2$  increases

rapidly with energy and passes through  $\frac{1}{2}\pi$  at a "resonance" energy  $E_r$ . It is clear from eq. (3) that at this energy the scattering cross section  $|t|^2$  is a maximum. In order to indicate how the resistivity depends on the form of the d phase shift we write:

$$\eta_2(E_F) = \arctan \left( \frac{\Gamma}{E_r - E_F} \right), \quad (4)$$

where  $\Gamma$  is the half-width of the resonance. This approximation for  $\eta_2$  is good provided the Fermi energy  $E_F$  is close to  $E_r$ . If the s and p phase shifts are small, then only the d contribution is important in eq. (3). The integral in eq. (1) can then be evaluated (approximately) because the integral is heavily weighted towards backward scattering, i.e.  $q \approx 2K_F$ , and the resistivity has the form

$$\rho \approx \frac{30\pi^3 \hbar^3}{m e^2 \Omega_0} \frac{a(2K_F)}{K_F^2} \frac{\Gamma^2}{E_F(\Gamma^2 + (E_r - E_F)^2)}. \quad (5)$$

The resistivity depends strongly on the width of the resonance, the position of the Fermi energy relative to the resonance energy and the radius  $K_F$  of the Fermi sphere. We have taken the Fermi velocity  $V_F$  equal to  $\hbar K_F/m$ , the usual free-electron approximation. To make first-principles calculations of the resistivity, one needs the appropriate electron-ion potential, the Fermi energy in the metal, information about the liquid structure factor and a prescription for evaluating the Fermi radius  $K_F$ .

Although there are many approximations and assumptions inherent in this simple theory (see DREIRACH *et al.*, 1972), it does appear to give a good understanding of the electrical resistivity in liquid noble metals, iron, nickel and many alloys.

## 3. Details of the calculations

In order to evaluate the phase shifts which go into eq. (3) for the scattering amplitude, we need a method for constructing the electron-ion potential in a liquid metal. The method adopted in the present work was the so called "muffin-tin" model which is usually employed in energy band structure calculations in solids. A "muffin-tin" potential is one in which the potential is taken to be spherically symmetrical within a sphere of radius  $R_{MT}$  centred around a given atom (in the solid or liquid). Outside of this radius  $R_{MT}$ , the potential is set equal to a constant,  $E_{MTZ}$ . The radius  $R_{MT}$  is usually

taken to be half the nearest-neighbour distance.  $E_{\text{MTZ}}$  is taken as the effective energy zero in the metal.

The actual construction of a muffin-tin potential is based on the MATTHEISS (1964) prescription of overlapping Hartree-Fock-Slater neutral atom charge densities. The total charge density  $f(\mathbf{r})$  can be written as:

$$f(\mathbf{r}) = f_0(\mathbf{r}) + \sum_{i \neq 0} f(\mathbf{r} - \mathbf{R}_i), \quad (6)$$

where  $\mathbf{R}_i$  is the position of an atom neighbouring the central atom  $i = 0$ . For liquid iron we assumed that the atoms were arranged in the bcc structure with a lattice parameter  $a$  corresponding to the density of the liquid, i.e.

$$\begin{aligned} \Omega_0 &= \frac{1}{2}a^3, \\ R_{\text{MT}} &= (\frac{1}{4}\sqrt{3})a. \end{aligned} \quad (7)$$

The coordination number of normal liquid iron near its melting point is  $\approx 9$  (WASEDA and SUZUKI, 1970; RUPPERSBERG and SEEMAN, 1966), which is not very different from the corresponding value of 8 for the bcc lattice. The total charge density should not be very sensitive to small changes in the coordination number or indeed to changes in the positions of atoms further away than the nearest neighbours. The electron-ion potential is obtained by solving the appropriate Poisson equation. Some average of the electron exchange interaction has to be included, and this has been done using a form of the Slater free-electron approximation; for details see DREIRACH *et al.* (1972) and the references therein.

The Fermi energy  $E_F$  can be calculated at each density using the method given by DREIRACH (1971). We write

$$E_F = E_b + \frac{\hbar^2}{2m^*} K_F^2, \quad (8)$$

where  $E_b$  is the energy of the bottom of the conduction band,  $m^*$  is a constant effective mass which is independent of density.  $K_F$  is the Fermi radius given by the familiar free-electron result,

$$K_F^3 = 3\pi^2 Z / \Omega_0. \quad (9)$$

Here  $Z$  is the number of "valence" electrons which we have taken to be constant and equal to one for iron. A discussion of the physics behind this choice is given by DREIRACH *et al.* (1972). Eq. (8) assumes that the width of the conduction band,  $E_F - E_b$ , scales with

density  $\Omega_0^{-1}$  like a simple parabolic band. The energy of the bottom of the band can be calculated from a knowledge of the  $s$  phase shifts of the corresponding muffin-tin potential, while the effective mass  $m^*$  was evaluated from band structure data on solid iron (WOOD, 1962).

We calculated muffin-tin potentials at several densities using the method outlined above. The phase shifts  $\eta_l$  were calculated for several energies by numerically integrating the radial Schrödinger equation inside the muffin-tin sphere. In table 1, we list the calculated val-

TABLE 1

Parameters entering the evaluation of the scattering cross-section at different densities. Here  $\Omega/\Omega_0$  is the ratio of atomic volumes, with  $\Omega_0$  the atomic volume of normal liquid iron. The muffin-tin zero  $E_{\text{MTZ}}$  is measured with respect to atomic zero. The energies  $E_b$ ,  $E_r$  and  $E_F$  are measured with respect to  $E_{\text{MTZ}}$

Density (g/cm <sup>3</sup> )	$\Omega/\Omega_0$	$E_{\text{MTZ}}$ (Ry)	$E_b$ (Ry)	$E_r$ (Ry)	$E_F$ (Ry)	$\Gamma$ (Ry)
6.86	1	-1.420	0.060	0.527	0.632	0.070
7.92	0.866	-1.626	0.141	0.66	0.77	0.110
8.82	0.778	-1.794	0.220	0.77	0.896	0.150
9.00	0.763	-1.828	0.237	0.79	0.922	0.155
9.40	0.730	-1.903	0.276	0.838	0.98	0.180

ues of some relevant parameters which determine the scattering cross section for the conduction electrons. Although we do not use the "resonance" formulae (4) and (5) in the actual calculation of the resistivity, it is instructive to look at how the position and width of the  $d$  resonance changes with the variation of density because these have major influence on the resistivity. As the density increases, the muffin-tin zero  $E_{\text{MTZ}}$  gets progressively lower, and this is simply due to the increasing overlap of the neighbouring atomic charge densities or potentials. The energy of the bottom of the band  $E_b$  and the resonance energy  $E_r$  both increase on decreasing the atomic volume. The width  $\Gamma$  of the resonance is a strong function of density and increases rapidly with increasing density. This in turn implies that the  $d$  band in the corresponding metal will broaden with an increase in density.

To calculate the resistivity, we need to know the liquid structure factor  $a(q)$  at each density. There is little experimental information about this, but it is possible, however, to make reasonable estimates of the behaviour of  $a(q)$  using the hard-sphere model (ASHCROFT and LEKNER, 1966). In this model, the structure

factor has a simple analytic form which depends on only two parameters, the packing fraction  $p$  and the hard sphere diameter  $R$ . These parameters are related to each other as

$$R^3 = \frac{6\Omega_0 p}{\pi}. \quad (10)$$

For most liquid metals under normal pressure and at temperatures near the melting point, a good approximation to the experimental structure factor can be obtained using a value of  $p$  equal to 0.45. The same choice for iron reproduces the observed  $a(q)$  of WASEDA and SUZUKI (1970) quite closely.

We estimated the variation of  $a(q)$  with density by making use of the thermodynamic relation (ASHCROFT and LEKNER, 1966)

$$a(0) = \frac{(1-p)^4}{(1+2p)^4} = \frac{K_B T \beta}{\Omega_0}, \quad (11)$$

where  $K_B$  is Boltzmann's constant,  $T$  is the absolute temperature and  $\beta$  is the isothermal compressibility.

If we want to calculate the electrical resistivity of iron in the Earth's core, we must take into account the variation of both the temperature and the density, i.e., we should know the relevant equation of state. Given such information, we can calculate the compressibility  $\beta$ , solve for  $p$  in eq. (11) and hence construct the appropriate structure factor.

HIGGINS and KENNEDY (1971) have recently attempted to analyse the temperature, pressure and density distributions in the Earth's core. They find that the pressure-temperature conditions approximate the melting curve for iron. We have used their data to calculate the packing fraction for several densities.

#### 4. Results for the resistivity of liquid iron

The resistivity was calculated by performing the integral in eq. (1) and using the full  $t$  matrix of eq. (3). For pure iron at 1620 °C, we obtained a value of 172  $\mu\Omega \cdot \text{cm}$  for the resistivity, which is in reasonable agreement with the experimental value of 139  $\mu\Omega \cdot \text{cm}$ . This calculation employed the experimental structure factor of WASEDA and SUZUKI (1970). The results for the resistivity at different densities and temperatures, calculated using the procedure for the structure factor outlined above, are listed in table 2. We predict a decrease in resistivity as the pressure and temperature

increase. The trends in these results are in qualitative agreement with those of KEELER and ROYCE (1971), who carried out shock wave experiments on the resistivity of *solid* iron.

TABLE 2

Calculated values of the resistivity of pure iron for various points on the melting point curve

Density (g/cm <sup>3</sup> )	Temperature (°C)	Pressure (Mbar)	Resistivity $\mu\Omega \cdot \text{cm}$
8.0	2400	0.15	138
8.5	2800	0.25	134
9.0	3000	0.46	124
9.5	3300	0.69	98
10.0	3400	0.77	63

KEELER and ROYCE (1971) have also measured the electrical conductivity of pure iron at pressures of  $\approx 1$  Mbar and at temperatures above 3000 °C. They give a value for the resistivity of iron of about 57  $\mu\Omega \cdot \text{cm}$  at 1.4 Mbar, this pressure corresponding to that at the core-mantle interface. Since our calculations are based on the HIGGINS and KENNEDY (1971) temperature-density relation for the melting curve of iron, our results should not be compared *directly* with these high-temperature shock-wave data of KEELER and ROYCE (1971). Nevertheless, if we take the density of iron at the interface to be 10 g/cm<sup>3</sup> (as quoted by KEELER and ROYCE, 1971), then according to the melting curve given by HIGGINS and KENNEDY (1971) the corresponding pressure and temperature would be about 0.77 Mbar and 3400 °C, respectively. Our calculated value of the resistivity under these conditions is 63  $\mu\Omega \cdot \text{cm}$  which is close to the shock-wave result, although the latter corresponds to a pressure of 1.4 Mbar and a temperature of 3500 °C.

#### 5. Discussion

The magnetohydrodynamic theories of the origin of the geomagnetic field require that the magnetic Reynolds number should be much larger than unity. The accepted figure is about 100, and this imposes a lower limit on the magnitude of the electrical conductivity of the outer liquid core. This limit is about  $3 \times 10^3 \Omega^{-1} \cdot \text{cm}^{-1}$  (e.g., KEELER and ROYCE, 1971, and references therein). In other words, the resistivity should be less than about 330  $\mu\Omega \cdot \text{cm}$ . Clearly our calculated figure easily satisfies this requirement. Even allowing for in-

accuracies of, say, about  $\pm 10\%$  in the values of compressibility which determine the structure factors, this will alter the resistivities by about  $\pm 7\%$ . We have simplified our calculations by taking the valence  $Z$  to be a constant independent of density or temperature. If we allow for increases in the Fermi radius due to possible variation of  $Z$ , then the resistivity is only likely to increase by a factor of two at most.

The Earth's outer core almost certainly contains lighter elements in solution with iron. It has long been suggested that these elements might be nickel or silicon. Recently, BUSCH *et al.* (1971) have measured the resistivity of some liquid transition metals at normal pressures. They find that alloying iron with germanium increases the resistivity of pure iron ( $139 \mu\Omega \cdot \text{cm}$ ) to maximum of  $186 \mu\Omega \cdot \text{cm}$  at about 35 at. % of germanium. Silicon is expected to behave in much the same way as germanium. When gold is alloyed with liquid iron, the resistivity is increased by a few % and nickel should be similar in this respect.

Our simple model has been applied to various alloys of liquid noble and transition metals (DREIRACH *et al.* 1972) and can explain many features of the alloying behaviour. The model predicts that the alloying dependence of the resistivity is much the same for the liquids at high pressures as at normal pressures. We do not expect very large changes in the resistivity of iron in the outer core due to the presence of nickel or silicon in solution. This is contrary to STACEY's (1967) estimates, but it is in accordance with GARDINER and STACEY (1971). The experiments of KEELER and ROYCE (1971) at 1.4 Mb give results for the resistivity of Fe-20% Ni and of Fe-20% Si as  $94 \mu\Omega \cdot \text{cm}$  and  $182 \mu\Omega \cdot \text{cm}$ , respectively. Unfortunately, it is not known whether these alloys are solid or liquid. We are unable to make accurate estimates of the effect of sulphur on the resistivity of an iron core, but we would not expect any drastic increase to occur, i.e., the resistivity should not be greater than the lower limit of  $330 \mu\Omega \cdot \text{cm}$ .

At this conference, RUNCORN (1972) has suggested the possibility of a dynamo model for the magnetic field of the Moon. If one assumes a liquid iron core for the Moon in its earlier history, then one can probably estimate the electrical conductivity of such a core from

table 2 by assuming some values for the relevant density and temperature.

In conclusion, we would like to point out that our model can be applied to most liquid metals at normal or high pressures, and we feel that it might be especially useful in interpreting static high-pressure conductivity data.

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