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Resistance Anomalies in Some Rare-Earth Metals*

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It is shown that the anomalies observed in the resistance of the lighter rare-earth metals can be explained in form and order of magnitude by a simple model of the interaction between the conduction electrons and the f electrons which are tightly bound to each atom. The f electrons interact with the crystal field set up by the surrounding atoms, so that there is a Stark splitting of their energy levels. The extra resistance arises because ion cores with f electrons in different states present different cross sections to the conduction electrons, and also because the conduction electrons can knock ions from one state to another. All exchange effects are neglected.

I. INTRODUCTION

WITH the advance made in the techniques of separation of the rare earths,[1] considerable quantities of the pure metals of these elements have become available and a beginning has been made in the investigation of their remarkable properties. These are so complicated, however, that the problem of finding a general theory which explains all the properties appears very difficult. It therefore seemed worth while to consider a very specific problem and to see whether an explanation of the resistance anomalies occurring in the measurements of James, Levgold, and Spedding[2] on cerium, praseodymium, and neodymium could be explained on a simple model.

Some features of a reasonable model are readily suggested by the known properties of all the rare-earth metals. Measurements of their magnetic susceptibility[3,4] over a temperature range show that, with two notable exceptions (europium and ytterbium), the metals have a paramagnetism similar to that of the corresponding trivalent rare-earth ions in ionic crystals.[5] This, together with the great similarity displayed by all the metals in general metallic properties and crystal structure,[3] has lead to the belief that a good basic approximation for these substances is to consider that all the atomic electrons are tightly bound around the nuclei at the lattice points except three per atom which form the conduction electrons. The configuration of a free rare-earth atom is often $4f^n5s^25p^65d6s^2$ outside inner closed shells, where the $5d6s^2$ electrons are loosely bound and readily lost, to form the trivalent ion in chemical compounds, and become the metallic conduction electrons. This model accounts for the fact that the metals are similar to each other in all properties depending largely on these electrons but differ widely in the properties which depend on the inner $4f$ electrons as n varies from 0 to 14 along the series. Thus ignoring the closed shells of electrons on each atom the problem is essentially that of finding the eigensolutions for the conduction electrons and the f electrons taking all the interactions into account. The four most important considerations are as follows.

(1) The energy band structure for the conduction electrons is required for an understanding of the resistivity and to find a reasonable approximation for the eigenfunctions of these electrons in order to discuss the effects of their interaction with the $4f$ electrons. Measurements[2] show an extremely high resistivity of a magnitude ($\sim 10^{-4}$ ohm-cm) similar to that shown by other metals with three conduction electrons (e.g., Sc), due possibly to overlapping bands.

(2) The interaction between the f electrons on the various atoms is important because it is the most probable cause of the ferromagnetism exhibited by gadolinium and those elements following it in the second half of the series.

(3) The f electrons will interact with the crystalline electric field set up by the lattice, and there will be a Stark splitting of the energy levels of each individual trivalent ion, similar to that observed in crystalline salts of the rare earths.[6]

(4) The interaction between the f electrons and the conduction electrons will affect the conductivity, and also possibly the ferromagnetism in the way proposed by Zener.[7]

The importance of these various interactions is indicated by other measurements on the lighter rare earths which we are considering. They are found to have a magnetic susceptibility which obeys Curie's law down to quite low temperatures, and do not appear to be ferromagnetic or antiferromagnetic. Measurements of specific heat by Parkinson *et al.*[8] have shown that in the main the quantity is very similar in all four metals (La, Ce, Pr, and Nd). This is not surprising since the lattices and conduction electrons are the same in all

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[1] F. H. Spedding *et al.* See, for example, J. Am. Chem. Soc. **72**, 2349 (1950).

[2] James, Levgold, and Spedding, Phys. Rev. **88**, 1092 (1952).

[3] W. Klemm and H. Bommer, Z. anorg. u. allgem. Chem. **231**, 138(1937).

[4] M. F. Trombe, Ann. Physik **7**, 385 (1937).

[5] J. H. VanVleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

[6] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932).

[7] C. Zener, Phys. Rev. **81**, 440 (1951); **83**, 299 (1951).

[8] Parkinson, Simon, and Spedding, Proc. Roy. Soc. (London) **A207**, 137 (1951).

four. However, the last three have an extra specific heat, not present in La, which displays a number of maxima (a sharp one in cerium at 12°K, two in neodymium at 7.5 and 19°K, and a broad maximum at 65°K in praseodymium). The explanation proposed by Parkinson *et al.*[8] is that this extra specific heat is from Schottky anomalies due to the Stark splitting of the f electrons mentioned in (3). They find that (except in Pr) the agreement is not particularly good and that some of the specific heat maxima are sharp and appear to come from some cooperative phenomenon. This would probably arise from (2) and just possibly (4). It is not clear, however, that these specific heat anomalies are associated with the onset of ferro- or antiferromagnetism. In particular it may be noticed that the anomalies in the resistance which occur at about the same temperatures appear to be different in form from those which occur near the known Curie temperatures of ferromagnets like gadolinium.[9]

We therefore propose to consider the effect on the resistance of a metal in which the core electrons localized on each lattice point have a number of low-lying energy levels [arising from Stark splitting (3)] but to neglect the interaction between these f electrons. It is found that an extra resistance is introduced of a form which will explain the observed anomalies. Unfortunately any calculation including the cooperative effects of (2) and (4) to try and account for the form of the specific heat anomalies seems very difficult and will not be attempted here.

2. MECHANISM FOR EXTRA RESISTANCE

The extra resistance is found to arise from two causes, each of which gives an effect of the same order and with the same temperature dependence.

(a) The conduction electrons can be inelastically scattered off an ion which is knocked from one energy state to another by giving or taking energy from the motion of the conduction electron.

(b) At finite temperatures there will be ions in these various energy states arranged at random on the lattice points and these numbers will vary, of course, with temperature according to the Boltzmann distribution. Since ions in these states will present slightly different cross sections for the elastic scattering of the conduction electrons, this scattering and thus the resistance will vary with the population and with temperature.

We start with the simplest case. Let us suppose that the metal lattice, volume V, is composed of N ions which have two energy levels separated by an energy Δ. Then in equilibrium the Boltzmann distribution gives the number of atoms in the lowest state,

$$N_l = N/(1+d), \quad \text{where} \quad d = e^{-\Delta/kT},$$

and the number in the upper state,

$$N_u = Nd/(1+d). \tag{1}$$

We use the wave vector $\mathbf{k}$ to describe the states of the conduction electrons, and define a distribution function $f(\mathbf{k})$ such that the number of electrons whose wave vectors lie in the interval $d\mathbf{k}$ about $\mathbf{k}$ is

$$[2V/(2\pi)^3]f(\mathbf{k})d\mathbf{k}. \tag{2}$$

Following the usual discussion of resistivity[10] in terms of the Boltzmann equation, we require the rate of change in $f(\mathbf{k})$ with time due to interactions with the lattice denoted by $[\partial f/\partial t]_{\text{coll}}$. Now here $[\partial f/\partial t]_{\text{coll}}$ is the total change in f due to the excess of the number of electrons entering $\mathbf{k}$ over those leaving due to scattering of the ions making up the lattice, and if $W(\mathbf{k},\mathbf{k}')$ is the probability per unit time that an electron in state $|\mathbf{k}\rangle$ is scattered into state $|\mathbf{k}'\rangle$,

$$[\partial f/\partial t]_{\text{coll}} = \int \{W(\mathbf{k}',\mathbf{k})f(\mathbf{k}')[1-f(\mathbf{k})] - W(\mathbf{k},\mathbf{k}')f(\mathbf{k})[1-f(\mathbf{k}')]\}d\mathbf{k}', \tag{3}$$

where the extra factors weight the process to ensure that there was an electron in the initial state and a vacancy in the final state. Now if $\mathcal{H}_{el}$ is the Hamiltonian of interaction between the lattice and an electron, and $|N_u,\mathbf{k}\rangle$ denotes a state of the system in which N_u ions are in the upper state and the electron has wave vector $\mathbf{k}$,

$$W(\mathbf{k},\mathbf{k}') = \sum_{N_u,N_u'} \frac{2\pi}{\hbar} |\langle N_u\mathbf{k}|\mathcal{H}_{el}|N_u',\mathbf{k}'\rangle|^2 \rho(\mathbf{k}') \times \delta[E(N_u,\mathbf{k}) - E(N_u',\mathbf{k}')], \tag{4}$$

where $\rho(\mathbf{k}')$ is the density of energy levels at $\mathbf{k}'$ and the δ function ensures energy conservation.

There are two kinds of terms which contribute to the sum in (4). The first are those terms which have $N_u = N_u'$, i.e., those which represent elastic scattering mentioned as (b) above. Of course, if $N_u = 0$, the matrix element is zero for there can be no scattering by a perfectly periodic lattice. If $N_u \neq 0$, however, the potential seen by the electron is no longer exactly periodic. The situation is exactly equivalent to that of resistivity in disordered alloys previously discussed by Nordheim[11] and Mott.[12] Since the difference between atoms as seen by the conduction electrons is entirely in the angular dependence of the charge in the f shell it will be small and can be considered by Nordheim's approximation. In this case the interaction Hamiltonian $\mathcal{H}_{el}$ is written as the sum of two terms, one representing the interaction between the conduction electrons and the f electrons, and the other between them and the rest of the charge complex of the ions. This latter term gives zero because it is periodic with the lattice. The former

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[9] Levgold, Spedding, Barson, and Elliott, Revs. Modern Phys. **25**, 129 (1953).

[10] See, for example, A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1936).

[11] L. Nordheim, Ann. Physik **9**, 607 (1931).

[12] N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).

term can be written as a screened Coulomb potential,

$$\sum_n \frac{e^2}{|\mathbf{r}_n-\mathbf{R}|}\exp(-|\mathbf{r}_n-\mathbf{R}|/q)=\sum_n h_n, \tag{5}$$

by using the simplification of one f electron per ion, and letting the one on the ion at the nth lattice point $\mathbf{a}_n$ be at $\mathbf{r}_n$ from that point, while the conduction electron is at $\mathbf{R}$.

Then

$$\langle N_u,\mathbf{k}|\mathcal{H}_{el}|N_u,\mathbf{k}'\rangle=\sum_n\langle\psi_n,\mathbf{k}|h_n|\psi_n,\mathbf{k}'\rangle, \tag{6}$$

where ψ_n is the wave function of the f electron near the nth lattice point, which can be the eigenfunction associated with the lower or the upper state, $\psi(l)$ or $\psi(u)$. Remembering that the expression (6) was zero if all the lattice points were alike, we can write it

$$\begin{aligned}\sum_n{}_u[\langle\psi_n(l),\mathbf{k}|h_n|\psi_n(l),\mathbf{k}'\rangle\\ -\langle\psi_n(u),\mathbf{k}|h_n|\psi_n(u),\mathbf{k}'\rangle],\end{aligned} \tag{7}$$

where the summation is over those lattice points n where the electron is in the upper state. Then the square of the matrix element becomes

$$\begin{aligned}|\sum_n{}_u\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_n]|^2|\langle\psi_n(l),\mathbf{k}|h_n|\psi_n(l),\mathbf{k}'\rangle\\ -\langle\psi_n(u),\mathbf{k}|h_n|\psi_n(u),\mathbf{k}'\rangle|^2,\end{aligned} \tag{8}$$

and since the points in the sum are randomly distributed the first factor can be written $N_u(1-N_u/N)$ and so, calling the difference of the matrix elements A and using Eq. (1), (8) becomes

$$N|A|^2/(1+d)^2. \tag{9}$$

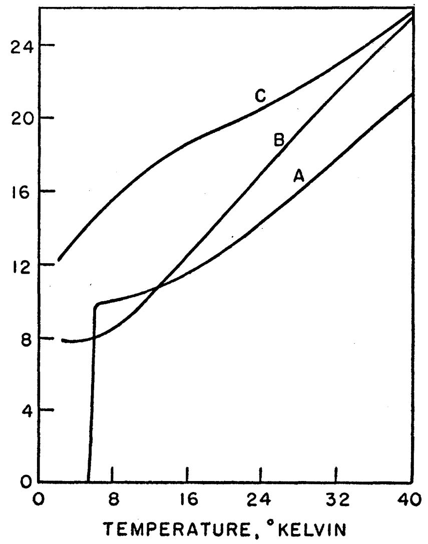

FIG. 1. Typical curves of resistivity *vs* temperature (after James *et al.*[2]). A. lanthanum, B. praseodymium, C. neodymium.

To proceed we must assume something about the conduction electron distribution function and energy. Making the simple assumption of isotropic effective mass m^* the usual treatment leads to a resistivity[10]

$$\rho=\frac{m^*}{ne^2\tau(k_0)}=\frac{NVd(2m^*)^{5/2}\epsilon^{1/2}}{(1+d)^2ne^2\hbar^4 4\pi}\int_0^\pi|A|^2(1-\cos\theta)d(\cos\theta), \tag{10}$$

where n is the number of conduction electrons per unit volume and k_0 is the length of the wave vector of electrons having the Fermi energy ϵ. ρ depends on temperature like $\operatorname{sech}^2(\Delta/2kT)$.

Since we are assuming that there is no interaction between the f electrons on different lattice sites, the only other terms of importance in (4) are those where $N_u-N_u'=\pm1$, and the problem is simply that of inelastic scattering of the conduction electrons off a set of atoms with two energy levels and (4) becomes

$$\begin{aligned}W(\mathbf{k},\mathbf{k}')=\frac{2\pi}{\hbar}\{|\langle\psi_n(l),\mathbf{k}|h_n|\psi_n(u),\mathbf{k}'\rangle|^2N_l\delta[E(\mathbf{k})\\ -E(\mathbf{k}')-\Delta]+|\langle\psi_n(u),\mathbf{k}|h_n|\psi_n(l),\mathbf{k}'\rangle|^2\\ \times N_u\delta[E(\mathbf{k})-E(\mathbf{k}')+\Delta]\}\rho(\mathbf{k}').\end{aligned} \tag{11}$$

In our approximation the matrix elements are the same [equal $B(\mathbf{k},\mathbf{k}')$, say], and substituting (11) into (3) we find

$$\begin{aligned}[\partial f/\partial t]_{\text{coll}}=\int\frac{2V|B|^2}{\hbar(2\pi)^2}\{[N_lf(\mathbf{k}')(1-f(\mathbf{k}))\\ -N_uf(\mathbf{k})(1-f(\mathbf{k}'))]\delta(E(\mathbf{k})-E(\mathbf{k}')+\Delta)\\ +[N_uf(\mathbf{k}')(1-f(\mathbf{k}))-N_lf(\mathbf{k})(1-f(\mathbf{k}'))]\\ \times\delta(E(\mathbf{k}')-E(\mathbf{k})+\Delta)\}d\mathbf{k}'.\end{aligned} \tag{12}$$

If we take $\Delta\ll\epsilon$, this expression yields τ exactly as the above and we get an additional resistance of the form:

$$\rho=\frac{NdV(2m^*)^{5/2}\epsilon^{1/2}}{(1+d)^2ne^2\hbar^4\pi}\int_0^\pi|B|^2(1-\cos\theta)d(\cos\theta), \tag{13}$$

which has exactly the same form as Eq. (10) except that $|A|$ has been replaced by $2|B|$. Thus the whole of the extra resistance depends on temperature like $\operatorname{sech}^2(\Delta/2kT)$.

These formulas can easily be generalized to include the case where there are an arbitrary number of energy levels for the f electrons; the energy of the ith being Δ_i and there being n_i atoms in this state at an arbitrary temperature T. If we further denote a matrix element like in Eq. (7) for elastic scattering off an ion in the ith and jth levels as in Eq. (20) by $B_{ij}(\mathbf{k},\mathbf{k}')$, the resistance arising from the first process is by analogy with Nordheim,[11]

$$\rho=\frac{V(2m^*)^{5/2}\epsilon^{1/2}}{ne^2\hbar^4 4\pi}\int_0^\pi\Bigl[\sum_i n_i|A_i(\mathbf{k},\mathbf{k}')|^2$$

$$-\frac{1}{N}|\sum_i n_iA_i(\mathbf{k},\mathbf{k}')|^2\Bigr](1-\cos\theta)d(\cos\theta),\quad(14)$$

and the second process gives

$$\rho=\frac{V(2m^*)^{5/2}\epsilon^{1/2}}{ne^2\hbar^4\pi}\int_0^\pi\sum_{i>j}\frac{n_in_j}{n_i+n_j}|B_{ij}(\mathbf{k},\mathbf{k}')|^2$$

$$\times(1-\cos\theta)d(\cos\theta).\quad(15)$$

3. APPLICATION TO THE RARE EARTHS

In Fig. 1 a curve of resistivity *vs* temperature is plotted to display the temperature dependence of this extra resistivity $\rho=\rho_0\,\mathrm{sech}^2(\Delta/2kT)$. With it is also plotted a typical curve for the resistivity arising from electron scattering by the lattice waves,

$$\rho=AT\Theta^{-1}G(\Theta/T),\quad(16)$$

where A is a constant, G the Grüneisen function,[13] and Θ the Debye temperature. The total resistivity of a hypothetical rare-earth metal where each ion has two energy levels separated by Δ would, on our model, be the sum of two such effects. A particular curve representing this sum when $k\Theta=10\Delta$, and $A=5\rho_0$, is also plotted.

In Fig. 2 typical experimental curves are shown for La, Pr, and Nd, taken from Spedding's data.[2] (Actually the results always varied slightly from sample to sample, and with treatment of sample, but for these three the curves are all similar. In the case of Ce the results varied much more, probably due to phase transitions.) It will be seen that, except for the superconducting transition in La (curve A) and a residual resistance in Pr (curve B), both resistivities are very similar in form to the typical curve for lattice scattering (II), if Θ is given the Debye value ~130°K [8] and $A\sim40\times10^{-6}$ ohm-cm. This agrees with our model since La has no f electrons, and in Pr the specific heat anomaly indicates that $\Delta/k\sim150$°K and so resistivity like I would not be appreciable below 30°K. On the other hand, the specific heat anomalies indicate that in Nd there is a $\Delta/k\sim15$°K (i.e., $\sim\Theta/10$) and we expect a curve like III in Fig. 1 (if we neglect the effect of higher levels), as is in fact observed (curve C). ρ_0 would have to be chosen $\sim10^{-5}$ ohm-cm to agree with experiment. The general form of the observed curves in Ce is the same as in Nd and here it appears $\Delta/k\sim25$°K so they can be explained in the same way. We have not considered them in detail because of the complication of the phase transition.

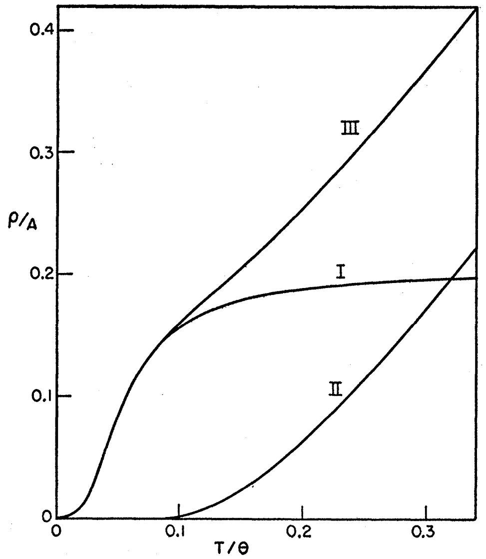

FIG. 2. Theoretical curves. I. The extra resistvity, $\rho=\frac{1}{5}A\times\mathrm{sech}^2(\Theta/20kT)$. II. Resistivity from lattice waves, $\rho=AT\Theta^{-1}\times G(T/\Theta)$. III. Sum of I and II.

It is therefore of interest to calculate the expected value of ρ_0 from our model. This reduces to evaluating the matrix elements A and B in Eqs. (10) and (13). By using the interaction Hamiltonian of Eq. (5), and assuming that the conduction electron wave functions can be written as normalized plane waves,

$$(1/\sqrt{V})\exp(i\mathbf{k}\cdot\mathbf{R}),\quad(17)$$

any A_i or B_{ij} can be written in terms of the integrals

$$\frac{1}{V}\int\int\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}]\psi^*(j)\psi(i)$$

$$\times\frac{e^2\exp(-|\mathbf{r}-\mathbf{R}|/2)}{|\mathbf{r}-\mathbf{R}|}d\tau_rd\tau_R,\quad(18)$$

where $\psi(i)$ is the wave function of the f electrons in the ith state and is a function of the positions $\mathbf{r}$ of these electrons. We assume for simplicity that each ion has one f electron and

$$\psi(i)=\frac{1}{(8!\rho^9)^{\frac{1}{2}}}r^3\exp(-r/\sigma)[\sum_{m=-3}^{3}a_i^mY_3^m(\theta,\phi)].\quad(19)$$

The electron wave function has, of course, the same radial dependence (here written as hydrogenic) but each state has a different angular dependence given by an appropriate linear combination of zonal harmonics of order 3. The actual values of the a_i^m are determined by the crystalline electric field, and the linear combinations for each i are normalized and orthogonal.

The integral in Eq. (18) can be separated by the transformation $(\mathbf{r}-\mathbf{R})\rightarrow\mathbf{R}$, $\mathbf{r}\rightarrow\mathbf{r}$ and becomes, writing

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[13] E. Grüneisen, Ann. Physik 16, 530 (1933).

$$\mathbf{k}-\mathbf{k}'=\mathbf{K},$$

$$\frac{e^2}{V}\int\frac{1}{R}\exp(i\mathbf{K}\cdot\mathbf{R}-R/q)d\tau_R\int\psi^*(j)\psi(i)$$
$$\times\exp(i\mathbf{K}\cdot\mathbf{R})d\tau_r. \quad (20)$$

The first integral is

$$4\pi q^2/(K^2q^2+1). \quad (21)$$

Considering the second integral we expand $\exp(i\mathbf{K}\cdot\mathbf{r})$ in a series of spherical harmonics:

$$\exp(i\mathbf{K}\cdot\mathbf{r})=\sum_l i^l(2l+1)j_l(Kr)\sum_{m=-l}^{+l}\frac{(n-|m|)!}{(n+|m|)!}$$
$$\times Y_l^m(\theta,\phi)Y_l^{-m}(\theta_K,\phi_K), \quad (22)$$

where θ_K, ϕ_K are the angles of $\mathbf{K}$ in spherical polars. Because of the angular dependence on θ of Eq. (19), it is easy to show that only the $l=0$, 2, 4, 6 terms contribute to the integrals. Further one can show that the integral arising from the $l=0$ term is zero unless $i=j$ and independent of i if $i=j$. Therefore the matrix element A which is the difference of two such integrals, and B where $i\neq j$, arise from terms $l=2$, 4, 6 only and are of the same order of magnitude. Even with these simplifications the integrals unsolved are very laborious, and it is not worth while to pursue them for an order of magnitude calculation such as this.

We therefore proceed with a rough numerical estimate. We assume $K\sigma\ll 1$, which is fairly reasonable if the f electrons are deeply seated on the ion cores, and $\mathbf{k}$, $\mathbf{k}'$ are wave vectors at the top of a Fermi distribution of essentially free electrons. Further, in choosing as an example two states whose wave functions are like Eq. (19) with an angular dependence Y_3^0 and Y_3^2, respectively, we find for the $l=2$ term

$$B_{ij}=\frac{4\pi\rho^2e^2}{(K^2q^2+1)V}\cdot\frac{K^2\sigma^2}{4}(3/5)^{\frac{1}{2}}Y_2^2(\theta_K,\phi_K). \quad (23)$$

Averaging over all directions of $\mathbf{K}$ for a multiple crystal removes the angular dependence and remembering that in our processes $|\mathbf{k}|=|\mathbf{k}'|$, $K=2k\sin(\theta/2)$, we have

$$\int_0^\pi B^2(1-\cos\theta)d(\cos\theta)=\frac{48}{5}\int_0^2\frac{\pi^3\sigma^4q^4k^4e^4s^3ds}{V^2(2k^2q^2s+1)^2}, \quad (24)$$

where $2\sin^2(\theta/2)=s$. If we make a further assumption that $kq\ll 1$, we have

$$\rho_0=192\pi^2(2m)^{5/2}\epsilon^{1/2}\sigma^4q^4k^4e^2/5h^4 \text{ electrostatic units}, \quad (25)$$

which for $\sigma=q\sim 1$A, $1/k=(8\pi V/3N)^{\frac{1}{3}}\sim 7$A, is $\sim 10^{-6}$ ohm-cm. Of course the above approximations make this estimate very rough for it seems unlikely that plane waves are a good approximation for the conduction electrons. However it does demonstrate that the order of magnitude of the effects discussed here is the same as that of the observed anomalies.

It is interesting to note that the matrix element (23) has an angular dependence with respect to the crystal axes. This will remain true when the correct expression is calculated for A or B and arises because of the angular dependence of the f-electron wave functions. In a single crystal this ought to give rise to an anisotropy in the extra resistance, though this will of course always retain the same temperature dependence.

4. CONCLUSION

We have discussed a model of a metal where, besides the conduction electrons, there are other electrons not in closed shells tightly bound to each atom at a lattice point and shown the form of the extra term this introduces into the resistivity. It has also been shown that if such a term is added to the usual resistivity it will account for the curious temperature dependence of the resistivity of some rare-earth metals. A very rough calculation of the expected order of magnitude agrees with the observations. Therefore the model seems a good starting point for a general consideration of these metals, although for a complete discussion the cooperative interactions between the electrons will have to be taken into account.