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# Spatial carrier density modulation effects in metallic conductivity

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Lattice defects in a metal modify the conduction-band carrier density at the defect site. Thus transport, past the scattering caused by thermal lattice vibrations, becomes easier (or harder) in the region of changed carrier density. The resulting transport field inhomogeneities have been discussed in earlier work on electromigration. This paper discusses the effect on the electronic resistivity.

## I. INTRODUCTION

Defects in metals act as localized scattering centers, and also as localized modifiers of the conduction-band carrier density. In a series of discussions, of which we will, at this point, cite only the latest items[1,2] this author has investigated the effects of these spatially inhomogeneous disturbances on the spatial distribution of fields and currents. This work is based on concepts originally proposed in 1957,[3] but which remained unaccepted for almost two decades. Recent work in electromigration theory has, however, produced a number of discussions[4-7] which agree either substantially, or even completely, with this viewpoint. Outside of the electromigration theory community, however, these concepts are still unaccepted. This paper points out that the spatial variations are not only relevant for the driving force in electromigration but also influence the ordinary electronic transport coefficients.

This author's original analysis[3] was limited to the effects of the extra localized scattering action due to the defects, without regard to the changes in carrier density. In that case the extra field required to overcome the defect scattering is highly localized, but its space average is that given by more conventional theories. Thus, initially, no new answer for the resistivity was put forth, though other transport coefficients were left open to more serious questions. In recent publications, however, the additional effects due to a nonuniform carrier density were introduced, and these do lead to corrections in the ordinary electrical resistance. This correction has been implicit in previous publications, but is stated more explicitly in this note.

In a dilute alloy one tends to think of the solute as modifying the density of mobile carriers in the conduction band, and assumes that the average density, $\langle n\rangle$, is acted on by the average field, $\langle\vec{E}\rangle$. In the presence of spatial variations, however, $\langle\vec{E}n\rangle \neq \langle\vec{E}\rangle\langle n\rangle$. The left-hand side of this inequality, which corresponds to the acceleration effects of the electric field, is not properly represented by the average field acting on the total carrier density.

Metallic resistivities, in the simplest approximation, obey Matthiessen's rule. In this view the resistivity of the alloy is taken to be that of the pure metal, except for the addition of an extra temperature-independent contribution to the scattering probability. There are many reasons for deviations from Matthiessen's rule, though the theoretical literature has emphasized the fact that thermal scattering rates and defect scattering are not simply additive, if the two scattering operators have different characteristic functions. Other deviations from Matthiessen's rule relate to the modification of the lattice vibrations by the defect and to the modification of the mobile charge density by the defect. The effect discussed in this paper relates to the latter. We are, thus, discussing a modification in only one of the possible deviations from Matthiessen's rule. As a result it may not be very directly relatable to experiments. Our point is, instead, made largely to demonstrate that the spatial variations really do affect the resistance. More striking effects can be expected for other transport properties. In view of the critical role of macroscopic spatial variations in magnetoresistance,[8] for example, one can also expect the microscopic variations to be important.

Let us first, briefly, consider a one-dimensional system which, within a semiclassical approximation, can be treated exactly.[9] In that case, near a defect, the density of electrons $n(x)$, and perhaps the Fermi-surface relaxation time $\tau$[11], are functions of position. A very naive approach might simply ignore the rapid spatial variation of $n$ and $\tau$, when compared with the mean free path, and calculate a resistance for the whole sample by integrating the local field, calculated according to $E(x)=i/\sigma(x)$. While such a field distribution is incorrect it was, in fact, shown in Ref. 9 that the integrated (or averaged) field value, calculated from this "naive" field, was exact. Thus the voltage drop $V$ is given by $\int i dx/\sigma \sim \int dx/n$, in the presence of a spatially varying $n$. The averaged or measured resistivity

thus varies as $\langle 1/n \rangle$, where the angular brackets denote spatial averaging. The conductivity thus varies as $\langle 1/n \rangle^{-1}$, which is not identical with $\langle n \rangle$. If the fluctuations in $n$ are small compared to $n$, this distinction is unimportant. In the vicinity of a defect, however, the carrier density modulation is not small, and thus the effect of the defect on $\langle 1/n \rangle^{-1}$ should be distinguishable from that on $\langle n \rangle$.

## II. THREE-DIMENSIONAL CASE

The three-dimensional case is more complex. In one dimension the continuity of current requires a separate momentum balance, for each volume element, between acceleration by the field on one hand and scattering on the other. In three dimensions this is no longer required, a localized scatterer can provide a region in which there is a net momentum loss. Indeed, this is the result found in the analysis of Ref. 3, and subsequently elaborated.[10] It was shown that if the defect caused a momentum loss $d\vec{P}/dt$, by scattering the incident carriers, then a localized dipole moment $\vec{p} = (4\pi e n_0)^{-1} d\vec{P}/dt$ is established. In this case $n_0$ is the density of carriers unperturbed by the lattice defect. Reference 3 did not take into account the effects of carrier density perturbations. This result can, in fact, be derived very easily without the complex analysis of Ref. 3 if we are willing to accept the fact that the residual resistivity field (i.e., the additional field required to maintain the average current upon introduction of the scatterer) comes in the form of a set of dipole fields. The extra field $\vec{E}_D$, associated with overcoming the defect scattering, must produce a rate of momentum gain, in the electron gas, which equals the rate of momentum loss due to the scatterers

$$-\vec{E}_D e n_0 = d\vec{P}/dt . \tag{1}$$

If the field $\vec{E}_D$ is composed of dipole fields then $\vec{E}_D = -4\pi N \vec{p}$, where $\vec{p}$ is the dipole moment and $N$ the dipole density. Thus $\vec{p} = (4\pi e n_0)^{-1} d\vec{P}/dt$, as already stated.

In the original discussion of Ref. 3, this result was derived by actually following the electrons incident on the scatterer, through their subsequent motion, as schematically illustrated in Fig. 1. The resultant charge pile-up was then screened in a self-consistent manner. Note that the flux coming out of the scattering volume quickly sorts itself out according to the scattered direction of motion, a circumstance which was rediscovered and emphasized by Das and Peierls.[11] The resulting charge pile-up (both before screening, and after) is thus only a function of the carrier distribution, in velocity, emanating from the scatterer, as long as we are not too concerned with the fine details very close to the scatterer. Therefore the net dipole moment produced depends only on that velocity distribution. The exact spatial distribution of the source charges for that dipole does, of course, still depend on the finer details of the scattering potential.

Since the dipole moment depends only on the emerging velocity distribution, it follows that the exact physical mechanism producing a local perturbation in the emerging velocity distribution does not have to be taken into account. Thus if deviations in $n$ cause a change in the emerging velocity distribution, we can calculate the resultant dipole from that distribution. This is the approach we shall invoke. Thus Eq. (1) holds, regardless of the physical cause for $d\vec{P}/dt$.

Let us now ask what the value of $d\vec{P}/dt$ is, as caused by spatial nonuniformities in the carrier density. To do this we shall, for the moment, assume that the effects of localized scattering, as discussed in the original residual resistivity dipole theory,[3] are completely separable from the effects of carrier density variation. Thus we explicitly consider the interaction of the carrier density variation with the thermally induced lattice scattering, but ignore the higher-order interaction between the extra (or deficit) carriers introduced by the defect, and the scattering field of that same defect. We shall return to this subject in the Appendix, to estimate the error involved. The rate of field driven momentum generation in a volume $V$ is given by $-e\int_V n\vec{E}\,d\tau$. If we take $n = n_0 + \delta n$, where $n_0$ is the unperturbed density, and take $\vec{E} = \vec{E}_0 + \delta\vec{E}$, where $\vec{E}_0$ is the uniform field due to charges far away from the lattice defect in question, then

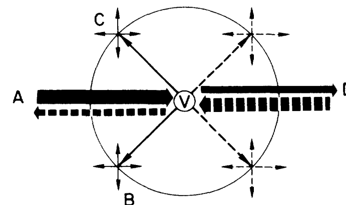


FIG. 1. Electrons in excess of the equilibrium concentration arrive from the left, as shown by heavy arrow A, and are partially transmitted, as shown by arrow D, and are partly scattered, by the perturbation potential V. The scattered excess moves away, ballistically, and is subsequently scattered again, by lattice vibrations, as indicated at B and C. The deficit electrons, incident from the right, and symbolized by dashed arrows, go through a similar history. The excess and deficit eventually diffuse together and recombine.

$$\int_V (n\vec{E})\,d\tau = \int_V (n_0\vec{E}_0 + n_0\delta\vec{E} + \delta n\vec{E}_0 + \delta n\delta\vec{E})\,d\tau. \tag{2}$$

The term in $n_0\vec{E}_0$ is not an inhomogeneity; it is balanced by lattice scattering of the original unperturbed current flow. $\delta\vec{E}$ exists as a result of the dipole formation, otherwise it would vanish. Thus the term $n_0\delta\vec{E}$, representing the interaction of the locally established dipole field with the unperturbed carrier density, is already taken into account in the derivation of Eq. (1), as part of $\vec{E}_D$, and is not a part of the excess local momentum generation on the right-hand side of Eq. (1). (This point was handled incorrectly in a closely related earlier discussion,[12] and subsequently corrected in a footnote in Ref. 1.) Now not all of the extra (or deficit) momentum generated in the area of carrier density perturbation will leave the volume of that lattice defect. The force field of the defect will cause deflection, and thus reduce the externally apparent effects. For the moment we will, as already indicated, neglect this and return to it in the Appendix. Thus omitting the first two right-hand terms in Eq. (2) we find

$$\vec{p} = (4\pi n_0)^{-1}\left(\vec{E}_0\int \delta n\,d\tau + \int \delta\vec{E}\delta n\,d\tau\right). \tag{3}$$

Let $\int \delta n\,d\tau$ be denoted by $Z$. Thus Eq. (3) becomes

$$\vec{p} = (4\pi n_0)^{-1}\left(\vec{E}_0 Z + \int \delta\vec{E}\delta n\,d\tau\right). \tag{4}$$

The final right-hand term is quadratic in the perturbation and, just conceivably, less critical. If $\delta n$ were constant and nonvanishing over a sphere of radius $a$ we would have, for the final right-hand term of Eq. (4),

$$\int \delta\vec{E}\delta n\,d\tau = Z(\tfrac{4}{3}\pi a^3)^{-1}\int \delta\vec{E}\,d\tau. \tag{5}$$

The integral of a dipole field over a sphere centered about the dipole and including all of the dipole source charges is $-4\pi\vec{p}/3$. Thus Eq. (5) becomes

$$\int \delta\vec{E}\delta n\,d\tau = -\vec{p}Z/a^3. \tag{6}$$

Unfortunately, however, $\delta n$ is not constant, nor is it clear that the sphere of radius $a$, which includes the region of static carrier density perturbations also includes all the dipole source charges. In fact the dipole source charges will extend, by at least a screening length, beyond the range of the scattering potential. To represent these geometrical uncertainties let us generalize Eq. (6) to

$$\int \delta\vec{E}\delta n\,d\tau = -\beta\vec{p}Z/a^3, \tag{7}$$

with a coefficient $\beta$ of order unity. Equation (7) can be substituted in Eq. (4). Solving the resulting equation for $p$ yields

$$\vec{p} = \vec{E}_0 Z/(4\pi n_0 + \beta Z/a^3) = (\tfrac{3}{4}\pi)Z\vec{E}_0/(3n_0 + \beta\delta n). \tag{8}$$

The field $\delta\vec{E}$ produced by $\vec{p}$, if $\vec{p}$ arises from a uniformly polarized region of volume $V$, is $\delta\vec{E} = -4\pi\vec{p}/3V$. Thus

$$\delta\vec{E} = -(Z/V)\vec{E}_0/(3n_0 + \beta\delta n). \tag{9}$$

If we now identify $V$ with the volume $\frac{4}{3}\pi a^3$ over which the charge $Z$ is spread, Eq. (9) becomes

$$\delta\vec{E} = -\delta n\vec{E}_0/(3n_0 + \beta\delta n). \tag{10}$$

As $\delta n$ in Eq. (10) is allowed to approach infinity, $\delta\vec{E}$ has to approach $-\vec{E}_0$. Thus the only value of $\beta$ which is consistent with all of our geometrical approximations is $\beta = 1$.

The increase in space average field caused by the dipoles of Eq. (8) is $-4\pi N\vec{p}$, where $N$ is the density of dipoles. Thus the increase in resistivity is

$$\delta\rho = -4\pi Np/\sigma_0 E_0; \tag{11}$$

$\sigma_0$ is the unperturbed conductivity. We will limit our concern to a dilute array of defects. In that case the distinction between the space average field, and the field that is effective as $\vec{E}_0$ in Eq. (8) can be neglected. Subtleties of this latter sort were the detailed concern of an earlier paper.[13] Equations (11) and (8) yield

$$\delta\rho/\rho_0 = -3NZ/(3n_0 + \beta\delta n). \tag{12}$$

The right-hand side numerator of Eq. (12) contains $NZ$, the defect charge per unit volume. This can also be written as $x\delta n$ where $x$ is the volume fraction occupied by the defects. Thus

$$\delta\rho/\rho = -3x\delta n/(3n_0 + \beta\delta n). \tag{13}$$

If we take $\beta = 1$ this becomes

$$\delta\rho/\rho = -3x\delta n/(2n_0 + n), \tag{14}$$

with $n = n_0 + \delta n$.

## III. COMPARISON TO MACROSCOPIC INHOMOGENEITY

The preceding section gave an approximate solution for the case where the carrier density inhomogeneity extends over a region small compared to the mean free path. At the other extreme we can consider a region large compared to the mean free path, and apply macroscopic

theory, i.e., apply $\vec{i} = \sigma\vec{E}$ locally. We can approach this limit, not only by making the inhomogeneity very large, but instead by making the background or lattice scattering very intense. In this latter case, however, we must also assume that the screening length is short enough (due to a high carrier density). Large space charges can then be piled up, and thus the field can change fast enough, in accordance with $\vec{i} = \sigma\vec{E}$.

In this macroscopic case the change in resistivity is given, for small $x$, by[14]

$$(\rho - \rho_0)/\rho_0 = -3x(\sigma_1 - \sigma_0)/(\sigma_1 + 2\sigma_0). \quad (15)$$

$\rho_0 = \sigma_0^{-1}$ characterizes the unperturbed material, $\sigma_1$ is the conductivity of the inclusion, and $x$ the volume fraction of inclusion. If we assume that $\sigma_1/\sigma_0 = (n_0 + \delta n)/n_0$, then Eq. (15) becomes

$$(\rho - \rho_0)/\rho_0 = -3x\delta n/(2n_0 + n_1). \quad (16)$$

This is identical to the result in Eq. (14). Thus under the assumption $\beta = 1$, a naive macroscopic theory will give the correct resistivity change, as it did in the more exactly treated one-dimensional case.[9] If $\beta$ is not exactly unity, the naive theory and the correct theory still behave qualitatively similarly. The $\beta\delta n$ term in the denominator of Eq. (13) represents the effect of the spatial correlations between field and carrier density. If $\delta n > 0$, for example, the field is reduced in the carrier rich region. This de-emphasizes the role of $\delta n$ and thus $\delta\rho/\rho_0$ is smaller in magnitude than $x\delta n/n_0$.

Note that the similarity between the large and small inhomogeneity is limited to the electric field distribution and the resistance. The disturbances in carrier distribution are very different for the two cases. For the macroscopic inhomogeneity the geometrical scale is set by the physical size of the defect, whereas in Fig. 1 it is determined by the mean free path.

## IV. ELECTROMIGRATION IMPLICATION

We return here to the implication of Eq. (15) for electromigration. The driving force, per unit volume, has been shown to be[1,4,6,15]

$$\vec{F} = -\vec{E}_T e n_0(\rho - \rho_0)/\rho, \quad (17)$$

where $\vec{E}_T$ is the average field in the alloy. Substituting from Eq. (12) we find a force, per impurity

$$\vec{F}/N = -\vec{E}_T Ze3n_0/(3n_0 + \beta\delta n). \quad (18)$$

This is a force which is related to the change in $\rho$ produced by the carrier density changes and is unrelated to any additional scattering introduced by the impurity. The mere fact that Eq. (18) gives a nonvanishing contribution shows that the analysis of Bosvieux and Friedel[16] is incorrect. Their theory only allowed a force related to the defect scattering action. The deviations in charge, from the perfect lattice were "screened," in the Bosvieux-Friedel treatment, leading to the absence of a "direct" force. Huntington's contrasting analysis,[17] however, which leads to a complete absence of screening, and thus to a direct force $-\vec{E}_T Ze$, is also incorrect. The direct force deviates from that value, as shown in Eq. (18), because the local field, seen by the bare defect ion (i.e., the ion and its tightly bound electrons, without any conduction band charges) is not $\vec{E}_T$, but deviates from that by $\delta\vec{E}$, as given in Eq. (9). We stress this fact here because in the otherwise definitive and perceptive treatment by Sham,[4] we find "The formula for the effective force is just that of Fiks and of Huntington and Grone." Later on in Sham's paper[4] it is, however, pointed out, in connection with conductivity modulation effects, that, "An... evaluation of such terms is, however, beyond the scope of this paper." It is of course just these conductivity modulation effects which we have treated in this paper, and which do change the "direct force."

## V. CONCLUSION

It is hoped that this discussion, despite its very crude approximations, has made it clear that spatial variations, about localized scatterers, do enter into electronic transport theory. Hopefully a more refined theory, based on diagrammatic techniques, can subsequently elaborate the role of the basic physical effects that we have invoked. It should also be stressed that while we have in this paper, as well as in its predecessors, stressed the metallic case, closely related questions can arise in other transport problems, e.g., in semiconductors or in phonon transport. The metallic case is particularly simple, since in that case not only the carrier flux, but also the electric field, can be very nonuniform with the electric field exhibiting a particularly close analogy to a macroscopic inhomogeneity. But even in other cases, an analog to Fig. 1 can be expected to apply.

## APPENDIX: INTERACTION OF DEFECT DENSITY WITH DEFECT SCATTERING

Up to now we have referred to two contributions to localized fields. One consists of the residual resistivity dipole and other closely related terms.[5] These terms arise from the scattering action of the defect acting on the acceleration induced in a uniform electron gas. The other term, the car-

rier density modulation term, allows for the spatial nonuniformity of the electron gas when subject to acceleration by an electric field. In Sec. II this was analyzed under the assumption that this acceleration was opposed only by a spatially uniform thermal scattering. The missing interaction between the nonuniform carrier density and scattering by the same defect was only briefly mentioned in Sec. II. There it was pointed out that as a result of this neglect we would be overestimating carrier density modulation effects. This Appendix is devoted to an estimate of these neglected higher-order interactions. This estimate carries our semiclassical approximation up to, or beyond, its limit of plausible applicability, and it is for this reason that these considerations have been placed in an Appendix.

Let us consider a situation in which the analysis of Sec. II applies: Carrier density inhomogeneities exist, but the scattering is only thermal scattering. Then assume that the defect scattering is turned on, in the presence of the current distribution as calculated in Sec. II. A residual resistivity dipole[3] is then generated; however, the incident current for this dipole is not the current far from the obstacle, but the perturbed current of Sec. II.

What is this perturbed current? The rate of excess local momentum generation $-d\vec{P}/dt$, is given by $-4\pi e n_0 \vec{p}$, with $\vec{p}$ given by Eqs. (4) and (8). This excess momentum is taken to be generated uniformly in the region of the defect. The carriers which have been accelerated stay within the defect volume while they continue to travel from the point of acceleration to the surface of the obstacle. We assume that the obstacle is a sphere of radius $a$. Elementary geometrical considerations show that the average value of this distance is $2a/3$. Thus the excess momentum, once generated, stays in the defect volume for a time $2a/3v$, where $v$ is the Fermi-surface velocity. Thus the extra momentum within the sphere is

$$(2a/3v)(-d\vec{P}/dt) = -8\pi e n_0 \vec{p} a/3v . \tag{A1}$$

To convert this to a current density we must multiply by $-e/m$ to convert momentum to electrical current, and then divide by the volume of the sphere $\frac{1}{3}(4\pi a^3)$ to yield a density. Thus, within the sphere, the current density change, $\delta\vec{j}$, is given by

$$\delta\vec{j} = 2e^2 n_0 \vec{p}/mva^2 . \tag{A2}$$

Thus the current density at the defect site is $\vec{j}_0 + \delta\vec{j}$, with $\vec{j}_0$ the current far from the obstacle. This is then, roughly, the current incident on the scattering field of the obstacle. Admittedly this is an approximation in which we are pushing our geometrical simplification to an extreme. The resultant resistivity dipole will be that calculated in the absence of carrier density modulation effects, multiplied by $(j_0 + \delta j)/j_0$. It is the departure from unity in this multiplier, $\delta j/j_0$, which represents the cross effect we are analyzing. Thus the contribution of the cross effect, $\rho_c$, to the resistivity is $\rho_r \delta j/j_0$, where $\rho_r$ is the residual resistivity. Hence, from Eq. (A2)

$$\rho_c = 2e^2 n_0 p \rho_r / mva^2 j_0 . \tag{A3}$$

The dipole moment $p$ appearing above can be replaced through Eq. (11), $\delta\rho = -4\pi N p/j_0$, with $N$ the density of defects. Thus

$$\rho_c = -\rho_r \delta\rho e^2 n_0 / 2\pi N m v a^2 . \tag{A4}$$

Now $\sigma_g = \pi a^2$ is the geometrical cross section of the obstacle and it can be used to define an electronic relaxation time

$$\tau_g = (N\sigma v)^{-1} = (N\pi a^2 v)^{-1} . \tag{A5}$$

This in turn yields a resistivity $\rho_g$ through

$$\rho_g = n_0 e^2 \tau_g / m = n_0 e^2 / N\pi m v a^2 . \tag{A6}$$

$\rho_g$ is then the residual resistivity which would be found if the actual scattering cross section were replaced by the geometrical area. $\rho_g$ can be used to simplify Eq. (A4) to

$$\rho_c = -\tfrac{1}{2}\delta\rho(\rho_r/\rho_g) . \tag{A7}$$

We see first of all that $\rho_c$ is opposed in sign to $\delta p$, thus it reduces the effects we have calculated in Sec. II. We furthermore note that $\rho_r$ need not be small compared to $\rho_g$; thus the correction (A7) can be important.

An alternative and even more approximate approach gives some physical insight into the appearance of $\rho_g$ in Eq. (A7). Let $\vec{j}_0$ be the uniform current incident on the region of inhomogeneous carrier density, which at first is assumed to cause no extra scattering. This gives a change $\vec{j}_0 \delta\rho$ in the space average field, as discussed in Sec. II. Now consider, instead $\vec{j}_0$ incident on a scattering field which is associated with a residual resistivity $\rho_r$. The current flow in the volume of the scatterers is reduced by a factor roughly of the form $(1 - \rho_g^{-1}\rho_r)$. As $\rho_r$ is increased and the obstacle becomes impenetrable, the current must vanish. But this impenetrability is reached when $\rho_r \sim \rho_g$, leading to the factor $(1 - \rho_g^{-1}\rho_r)$, that we have just specified. Now in the presence of *this reduced current flow*, let the carrier density inhomogeneity and the thermal scattering be turned on. The dipole associated with carrier density

modulation can then be estimated as

$$\vec{j}_0(1-\rho_g^{-1}\rho_r)\delta\rho\,. \tag{A8}$$

The cross effects are contained in the term $\vec{j}_0\rho_g^{-1}\rho_r\delta\rho$, which is twice the expression given in Eq. (A7). Quantum mechanically, of course, a scattering cross section can be large compared to a geometrical cross section, if the spatial extent of the scattering potential is small compared to the wavelength. Thus we can see that the semiclassical reasoning given above is not very accurate. It is, on the other hand, not completely inapplicable. The Fermi wavelength is not large compared to the obstacle.

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