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Gravitation-Induced Electric Field near a Metal. II *

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It is shown that screening of the ionic lattice by conduction electrons is insufficient to account for the zero acceleration found in the experiment of Witteborn and Fairbank on the free fall of electrons within a metallic shield. A speculative suggestion is made for reconciling this conclusion with the results of the centrifuge experiment of Beams and the uniform-compression experiment of Craig.

I. HISTORICAL INTRODUCTION

The matters under discussion in this paper first arose in connection with proposed experiments on the free fall of electrons and positrons.[1] In order that the extremely weak force exerted by the earth's gravitational field on an electron be measurable, it is necessary that the electron be shielded from stray electric fields. This is accomplished by enclosing the experimental region in a vertical metal tube of circular cross section. However, it was suggested at an early stage[2] that earth gravity, acting on the metal, might produce an electric field within the tube which would complicate the interpretation of the experiment. A detailed quantum-mechanical calculation was then performed[3] which concluded that the gravitation-induced electric field within the tube is expected to be $-(mg/e)\hat{z}$, where m and $-e$ are the mass and charge of an electron, g is the acceleration of gravity, and $\hat{z}$ is a unit vector in the upward direction. This field just cancels the downward gravitational force on a free electron and doubles the downward gravitational force on a free positron.[4] The experiment, performed by Witteborn and Fairbank,[5] confirms this prediction for electrons. The measured acceleration is zero with an uncertainty of $\pm 0.09g$.

A different view of the theoretical situation was then presented by Dessler, Michel, Rorschach, and Trammell,[6] who argued that the differential compression of the ionic lattice would lead to an electric field roughly ten thousand times larger and in the opposite direction, a field of order $+(Mg/e)\hat{z}$, where M is the ionic mass. On the other hand, lattice compression effects were estimated to be negligible both in the original theoretical paper[3] and in a subsequent investigation.[7]

Herring[8] resolved this theoretical disagreement by showing how the reciprocity-relation approach of Schiff and Barnhill[3] can be extended to include ionic as well as electronic effects. He found that the first estimate of the lattice compression effect was too small, and that the large electric field[6] should be observed. Still more recently, however, Peshkin[9] has argued that the surface electrons shield the lattice ions to such an extent that they do not contribute appreciably, thus supporting his earlier result.[7]

Two further experiments have been performed. Beams[10] made use of a rapidly spinning rotor, in order to obtain accelerations much greater than can be obtained from earth gravity. He found electric fields of the order of those expected from the ionic effect. That a centrifugal accleration should produce the same kind of effect as a gravitational acceleration was shown by Barnhill.[11] The other experiment, performed by Craig,[12] applies a uniform stress to a piece of metal and measures the change in contact potential. The result obtained is in order-of-magnitude agreement with that predicted from the lattice compression effect. Harrison[13] has argued that this experiment is not strictly comparable with the others, since the stress is uniform, and suggests an alternative arrangement that would simulate differential compression.

The primary purpose of the present paper is to resolve the question of whether or not the surface electrons provide the high degree of shielding of the ions that is needed if the ionic effect is to be suppressed. Our conclusion that they do not is in agreement with Herring[8] and in disagreement with Peshkin.[9] Following this, a speculative suggestion is presented which is intended to reconcile the experimental results by Witteborn and Fairbank,[5] Beams,[10] and Craig[12] with each other and with the theory.

II. SHIELDING BY SURFACE ELECTRONS

After the analysis described in this section was completed, the author's attention was called to a preprint by Newns,[14] in which the dielectric response of an idealized metal is calculated beyond the Thomas-Fermi approximation. Newns's work is more general than that described here in that it takes account of space-time-dependent perturbations, but more special in that it represents the metallic surface by an infinite potential barrier; also, the present analytical approach is somewhat different from that of Newns. Because of these differences, we believe it is worthwhile to present a brief description of our calculation.

The metal is assumed to consist of a smoothed-out positive-ion density that is a function only of the coordinate x perpendicular to the surface and vanishes for $x > 0$, together with enough electrons to provide over-all electrical neutrality. Each of these electrons moves in an effective potential energy $V(x)$ that is the sum of its electrostatic interaction with all the other electrons and the positive ions, together with the exchange and correlation energies. The Schrödinger equation in atomic units is

$$[-\nabla^2 + V(x)]\,\psi_{\vec{K}}(\vec{r}) = K^2 \psi_{\vec{K}}(\vec{r}) \ ,$$

where $\psi_{\vec{K}}(\vec{r}) = u_k(x)\ \exp i(K_y y + K_z z)$,

$$K^2 = k^2 + K_y^2 + K_z^2 \ .$$

The effective potential $V(x)$ approaches zero as $x \to -\infty$ and V_0 as $x \to +\infty$. $u_k(x)$ satisfies the equation

$$\left(-\frac{d^2}{dx^2} + V(x)\right) u_k(x) = k^2 u_k(x), \qquad (1)$$

and can be chosen real since $V(x)$ is real. It is normalized such that

$$u_k(x) \to \sin(kx + \alpha_k) \ , \quad x \to -\infty \qquad (2)$$

where α_k is fixed by the requirement that $u_k(x)$ approach zero as $x \to +\infty$.

The electron number density is

$$n(\vec{r}) = n(x) = \pi^{-3} \int |\psi_{\vec{K}}(\vec{r})|^2 d^3K \ ,$$

where the integration is carried over a sphere of radius k_F, the Fermi wave number. The K_y and K_z integrations are readily performed, and lead to

$$n(x) = \pi^{-2} \int_0^{k_F} (k_F^2 - k^2)\, u_k^2(x)\, dk \ . \qquad (3)$$

The self-consistency condition now requires that $V(x)$ be the sum of an electrostatic part, which is the solution of Poisson's equation with the charge density derived from the positive-ion density and the electron density (3), together with an exchange plus correlation part which is a functional of $n(x)$. Such a calculation with a uniform ion density has recently been performed by Lang,[15] who made use of the work of Hohenberg, Kohn, and Sham.[16]

It is desirable at this point to review briefly the reciprocity-relation approach of Schiff and Barnhill,[3] which was extended by Herring[8] to include ionic effects. The calculation of the gravitation-induced electric field near a metal is performed in two stages. First, an infinitesimal test charge q is placed at the field point in the absence of the gravitational field, and the changes in the wave functions of the electrons and ions that are of first order in q are calculated. Second, the change in the expectation value of the gravitational potential energy that arises from the altered wave functions is computed. The desired electric field is then $1/q$ times that gradient of this energy. Schiff and Barnhill showed that the changes in the electronic wave functions give rise to the field $-(mg/e)\hat{z}$ inside a cavity or a long narrow tube, and estimated that the penetration of the field of the test charge was not enough to change the ionic wave functions sufficiently to alter this value appreciably. On the other hand, Herring showed that even a greatly attenuated penetration to the first ion layer is enough to deform the lattice so that the ionic contribution to the gravitation-induced electric field dominates the electronic contribution. This occurs through what Herring calls a "surface pinch": The test charge exerts oposite forces on the ionic lattice above and below the height of the test charge, and the elastic response of the lattice is such that its mass distribution is changed significantly.

It is apparent, then, that our main concern is to estimate the extent to which the electric field of an external test charge penetrates beneath the metallic surface. It is sufficient for our purpose to replace the test charge by a constant external electric field of strength E in the positive x direction since the yz dependence of the field of the test charge is not essential in calculating the penetration. We therefore change the effective potential $V(x)$ to $V(x)+v(x)$, where $v(x)$ approaches zero as $x\to-\infty$ and $(2E/e)(x-b)$ in a.u. as $x\to+\infty$, where b is as yet undetermined. This perturbation $v(x)$ alters the electron wave functions and changes the electron number density from $n(x)$ to $n(x)+\delta n(x)$; we neglect its effect on the ion density, which is permissible in a first-order calculation. The self-consistency condition then requires that $v(x)$ be the sum of an electronstatic part, which is calculated from $\delta n(x)$ through Poisson's equation, together with an exchange plus correlation part which is a functional of $n(x)$ and is proportional to $\delta n(x)$.

A typical electron wave function $u_k(x)$ is changed into $u_k(x)+w_k(x)$, and the wave equation (1) gives to first order

$$\left(\frac{d^2}{dx^2}+V(x)-k^2\right)w_k(x)=-v(x)u_k(x)\ . \tag{4}$$

We normalize u_k+w_k to unit amplitude when $x\to-\infty$, as in Eq. (2). Then the electron number density is given by (3) with u_k replaced by u_k+w_k, since the density of states and the value of k_F are determined by the properties of the metal far in the interior, which are unchanged when E is applied. Thus

$$\delta n(x)=(2/\pi^2)\int_0^k(k_F^2-k^2)u_k(x)w_k(x)\,dk \tag{5}$$

to first order.

Equation (4) is solved with the help of a symmetrical Green's function $G_k(x,x')$, which satisfies the inhomogeneous equation

$$\left(\frac{-d^2}{dx^2}+V(x)-k^2\right)G_k(x,x')=\delta(x-x')$$

and approaches zero as either of its arguments approaches $+\infty$. As is well known,

$$G_k(x,x')=-k^{-1}\bar{u}_k(x_<)u_k(x_>)\ , \tag{6}$$

where $x_<$ and $x_>$ are the lesser and greater, respectively, of x and x', and $\bar{u}_k(x)$ is the solution of Eq. (1) that is irregular at $+\infty$ and approaches $\cos(kx+\alpha_k)$ as $x\to-\infty$. We thus obtain

$$w_k(x)=-\int_{-\infty}^{\infty}G_k(x,x')v(x')u_k(x')\,dx'\ . \tag{7}$$

It is apparent that u_k+w_k does not have unit amplitude when $x\to-\infty$; however, since u_k and w_k are 90° out of phase, this amplitude differs from unity only by a quantity of second order in the perturbation, so that renormalization is unnecessary.

Substitution of (6) and (7) into (5) gives

$$\delta n(x)=(2/\pi^2)\int_{-\infty}^{\infty}F(x,x')\,v(x')\,dx'\ , \tag{8}$$

where $F(x,x')$ is symmetrical in its arguments and is given for $x<x'$ by

$$F(x,x')=\int_0^{k_F}(k_F^2-k^2)u_k(x)\,\bar{u}_k(x)\,u_k^2(x')\,\frac{dk}{k}\ . \tag{9}$$

Poisson's equation in a.u. is

$$\frac{d^2v_{es}(x)}{dx^2}=-8\pi\delta n(x)=-\frac{16}{\pi}\int_{-\infty}^{\infty}F(x,x')v(x')\,dx', \tag{10}$$

where $v_{es}(x)$ is the electrostatic part of $v(x)$. The exchange plus correlation part $v_{xc}(x)$ can be calculated approximately by assuming it depends only on the local electron density,[15] in which case it is equal to $\delta n(x)$ multiplied by a known function of $n(x)$. Now for positive increasing x, v_{xc} falls rapidly to zero while v_{es} increases linearly with x in a region in which $u_k^2(x)$ is still appreciable. For negative x and for x close to zero, v_{es} and v_{xc} are both small and of the same order of magnitude. Thus the dominant contribution to the integrand on the right-hand side of Eq. (10) comes from positive x where v_{es} is much larger than v_{xc}. We therefore approximate Eq. (10) by replacing v by v_{es} on the right-hand side:

$$\frac{d^2v_{es}(x)}{dx^2}=-\frac{16}{\pi}\int_{-\infty}^{\infty}F(x,x')\,v_{es}(x')\,dx'\ . \tag{11}$$

When Eq. (11) is solved, v_{es} may be substituted into (8) to estimate δn, which in turn can be used to find v_{xc}. In this way an approximate expression for $v=v_{es}+v_{xc}$ can be obtained.

It is important to note that the approximation of neglecting v_{xc} in comparison with v_{es} is much better in this situation than when dealing with the unperturbed potentials V_{xc} and V_{es} since as pointed out above there is a well-defined region in which v_{es} dominates v_{xc}. Also, it hardly need be stated that it is far easier to work with Eq. (11) than simultaneously with (10) and the equation that relates v_{xc} to δn.

Equation (11) resembles a homogeneous Fredholm equation, and this resemblance would be increased by performing a Fourier transformation. It might therefore be doubted that it has a solution for the particular value $-16/\pi$ of the coefficient of the right-hand side. However, the Fourier transformation cannot in fact be performed since $v_{es}(x)$ grows without limit for large positive x. Instead we can make the substitutions

$$\phi(x) = \frac{dv_{es}(x)}{dx}, \quad F(x,x') = -\frac{\partial^2 K(x,x')}{\partial x\,\partial x'} . \tag{12}$$

The second of Eqs. (12) can be integrated such that $K(x,x')$ is symmetrical in its arguments, and vanishes exponentially for large positive values and as an inverse power for large negative values; for $x < x'$ we put

$$K(x,x') = \int_{-\infty}^{x} \int_{x'}^{\infty} F(x_1,x_2)\, dx_1\, dx_2 . \tag{13}$$

We thus obtain the inhomogeneous Fredholm equation

$$\phi(x) = C + \lambda \int_{-\infty}^{\infty} K(x,x')\phi(x')\, dx', \quad \lambda = -16/\pi \tag{14}$$

where C is introduced as an arbitrary constant of integration. Equation (14) has a solution $\phi(x)$ that vanishes for large negative x and approaches a constant for large positive x, unless $\lambda = -16/\pi$ happens to be an eigenvalue of the kernel (13); we assume that this is not the case. $\phi(x)$ obtained in this way will be proportional to C, which must be chosen such that $\phi(x) \to 2E/e$ as $x \to +\infty$. The first of Eqs. (12) can then be integrated to give

$$v_{es}(x) = \int_{-\infty}^{x} \phi(x')\, dx' . \tag{15}$$

The inegration in (15) leads to the desired asymptotic form $(2E/e)(x-b)$ for $v_{es}(x)$ or $v(x)$ as $x \to +\infty$, and also serves to determine b.

III. NUMERICAL ESTIMATE

The availability of a self-consistent effective potential $V(x)$ and the corresponding wave functions $u_k(x)$ from the work of Lang[15] makes it possible to calculate the irrregular solutions $\bar{u}_k(x)$ and hence $F(x,x')$. One could then proceed to solve either of the integral equations (11) or (14) for v_{es} and δn, and thence obtain v_{xc} and finally $v(x)$. A somewhat less ambitious program would consist of assuming a plausible form for $V(x)$ and making use of the WKB forms for u_k and $\bar{u}_k$.[17] For the present purpose, it was felt to be sufficient to make a rough numerical estimate based on the $V(x)$ calculated by Lang for $r_s = 5$ or $k_F = 0.384$, using greatly simplified WKB solutions.

The classical expression for v or v_{es},

$$v_{es}(x) = 2Ex/e \qquad \text{for } x > 0,$$
$$v_{es}(x) = 0 \qquad \text{for } x < 0,$$

was substituted on the right-hand side of Eq. (11), and the left-hand side integrated once to obtain the electric field (neglecting v_{xc}) inside the metal. The result for the ratio of interior to externally applied electric field is ($r_s = 5$)

$$R(x) = 0.188\left(\int_z^{\infty} \frac{\sin t}{t}\, dt + \frac{\sin z - z\cos z}{z^2}\right), \tag{16}$$
$$z = 2k_F|x|$$

where $x < 0$. Equation (16) is plotted in Fig. 1, which shows the characteristic surface Friedel oscillations. While the field falls off rapidly with depth within the metal, the decrease is not nearly rapid enough to provide effective shielding of the ions from the test charge. Thus at a depth of 1 Å, which corresponds to $z = 1.45$, the field is only reduced to about one-eighth of the external field. This general behavior is in order-of-magnitude agreement with that found by Newns[14] using a different model.

IV. A SPECULATIVE SUGGESTION

There is evidently a clear discrepancy between the result of the Witteborn-Fairbank free-fall experiment[5] and theoretical expectation. There is also order-of-magnitude agreement of the Beams centrifuge experiment[10] and the Craig uniform-compression experiment[12] with each other and with the theory. Thus any theoretical suggestion that is intended to remove the first discrepancy must be designed not to be operative in the latter experiments.

What is required to account for the free-fall ex-

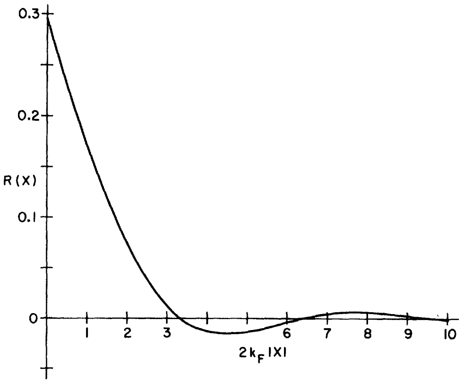

FIG. 1. Plot of the ratio $R(x)$ of the electric field within the metal ($x < 0$) to the externally applied field, for $r_s = 5$ or $k_F = 0.384$.

periment is a means for decoupling the surface layer from the substrate. We quote from two recent papers. "It seems likely that ionic effects are shielded out by a surface layer that does not share the gravitational deformation of the underlying metal, so that only the electrons in the surface layer contribute to the electric field within the tube."[18] "This suggests that it is possible to shield the stress-induced contact potential by placing over the sample surface an unstressed surface layer in electrical contact with the sample.... Such an unstressed surface might be prepared by attaching to the sample surface small conducting particles sufficiently far apart that no stress could be transmitted from particle to particle and yet close enough that the contact potential outside the surface would be controlled by the particles...it is possible that the specially prepared amorphous copper surface used by Witteborn and Fairbank may satisfy the requirements."[12]

We wish to argue that the surface layer cannot be solid, even if it is composed of disconnected small particles, so long as these particles are rigidly attached to the substrate. From the point of view of Dessler *et al.*[6] such particles would be deformed by the change in lattice constant of the substrate, since each would be attached by many neighboring lattice bonds. From the point of view of Herring[8] the "surface pinch" would be transmitted to the substrate by the particles.

Instead, we suggest that the surface layer in the free-fall experiment, which need only be a few atoms thick, is so constructed that it is electronically conducting but cannot support shear. It might consist of a continuous or broken-up fluid layer; or, as a modification of the quotation from Craig's paper given above, it might consist of disconnected small particles that are not rigidly attached to the substrate. Then from the Dessler point of view the surface layer, whether or not continuous, would not share the gravitational deformation of the underlying metal. From the Herring point of view there would be no "surface pinch" since this depends on rigid attachment to the substrate; the force on any macroscopically small element of the surface would be proportional to the square of the magnitude q of the test charge, rather than to q, so that the reciprocity relation would predict no electric field arising from the ions (see also the discussion in Appendix B of Ref. 8).

Assuming that such a surface layer is present in the free-fall experiment, we are left with the problem of explaining why it is not present, or at least not effective, in the centrifuge and uniform-compression experiments. There are several possible sources for the difference in the two classes of experiment: (a) The difference may arise from surface treatment. As mentioned by Craig, the amorphous copper surface used in the free-fall experiment may have a particulate character, which we now suggest may also be mobile. (b) The strains involved in the latter group of experiments are several orders of magnitude larger than in the free-fall experiment. It is possible that the surface layer is attached to the substrate in such a way that it is mobile for very small stresses but not for large stresses; for example, only a very small relative motion may be possible without developing a shear stress. (c) The mobile surface layer may be stable at 4.2 °K (free-fall experiment) but not at room temperature. Or it may be scoured off by molecular bombardment at atmospheric pressure (uniform-compression experiment) and at reduced pressure and high rotational speed (centrifuge experiment), but not at extremely low pressure and temperature (free-fall experiment).

In any event, it is likely that the results of Witteborn and Fairbank[5] cannot be understood without a radical departure from the usual picture of the metallic surface.

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Theory of Electronic Properties of Thin Films of *d*-Band Metals

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We have examined the changes in the nature of the d-band states in crystals of fcc transition and noble metals as the crystals become very thin. The calculated effects can be categorized as size effects and as surface effects. The size effects are the changes from states having a semicontinuous variation of energy with varying wave vector parallel to the small dimension to states having discrete energy values. These effects result from the loss of translational and cubic symmetry, and exist even when the overlap integrals are the same within the surface planes as within the interior planes of the crystal. The effects found are qualitatively different for single-crystal fcc films with ⟨100⟩ and ⟨111⟩ normals, respectively. Surface effects are changes in the electronic structure associated with changes of overlap integrals within the surface planes. We show how such changes lead to the existence of d-band surface states for a ⟨100⟩ film. For ⟨111⟩ films, there is an even more striking qualitative effect involving surface states. This is the appearance of surface states for one area of the two-dimensional Brillouin zone even when the overlap integrals within the boundary planes are the same as those within the interior planes of the film. We illustrate all these effects by calculations for the Γ_{12} bands (i.e., the bands corresponding to E-symmetry d atomic states), using realistic parameters for Ni with crystals 5 and 11 atomic layers thick. Finally, we discuss the prospects for experimental work – in particular, investigations of the density of states and of various anisotropic effects associated with the departure from cubic symmetry on going to a very thin film.

I. INTRODUCTION

In this paper, we examine the nature of the expected changes in the electronic structure associated with the d bands in fcc transition and noble metals on going to very thin crystals (i.e., single-crystal films). As one dimension of a crystal becomes very thin, we expect a change in the nature of the energy eigenstates corresponding to a change in the variation of energy with wave vector normal to the crystal surface from a semicontinuous band to discrete values. Also, depending on the surface conditions, surface states can appear, and the number of such states can be relatively much more important than for bulk solids. Going to a thin crystal also involves a fundamental change in the symmetry properties of a crystal. A very thin crystal of a cubic metal such as copper or nickel is no longer truly cubic, and this departure from cubic symmetry is reflected in the nature of the electronic states.

The above changes in electronic structure may have significant effects on various physical properties of a film which depend on the electronic density of states (e.g., optical properties and photoemission behavior). Qualitatively, the most striking effects will be the introduction of anisotropy, corresponding to the departure from cubic symmetry, into various properties. For example, the diagonal elements of the dielectric constant tensor, giving the optical absorption, no longer will be equal. Also, for cubic magnetic metals,