coordinate systems, are transformed to the coordinate system of Eq. (1) and added to yield the above result.

Maxwell's equations yield a solution for the propagation constant Γ given by

$$\Gamma^2=-\omega^2\epsilon\mu_0+j\omega\mu_0\sigma_{\mathrm{eff}}, \tag{2}$$

where ω is the frequency of an rf field **E**, ϵ is the dielectric constant, and σ_{eff} becomes

$$\boldsymbol{\alpha}\|\mathbf{B}: \quad \sigma_{\mathrm{eff}}=\tfrac{1}{2}(\sigma_{11}+\sigma_{22})\pm j[\sigma_{12}^2-\tfrac{1}{4}(\sigma_{11}-\sigma_{22})^2]^{\frac{1}{2}}, \tag{3a}$$

$$\boldsymbol{\alpha}\perp\mathbf{B}: \begin{cases} \sigma_{\mathrm{eff}}=\sigma_{33}, & \text{(3b)} \\ \sigma_{\mathrm{eff}}=\dfrac{\omega\epsilon(\alpha_2^2\sigma_{11}+\alpha_1^2\sigma_{22})-j(\sigma_{12}^2+\sigma_{11}\sigma_{22})}{\omega\epsilon-j(\alpha_1^2\sigma_{11}+\alpha_2^2\sigma_{22})}, & \text{(3c)} \end{cases}$$

where $\boldsymbol{\alpha}$ is the unit vector along $\boldsymbol{\Gamma}$. For longitudinal propagation, Eq. (3a), **E** is elliptically polarized normal to **B** and circularly polarized when $\sigma_{11}=\sigma_{22}$. Transverse propagation has two cases, (3a) corresponding to linear polarization with **E** along **B** and (3b) to elliptical polarization with $\mathbf{E}\perp\mathbf{B}$. The effective conductivities for **B** along the [001] direction for the eight and the [111] for the six ellipsoids are identical, and for $\boldsymbol{\alpha}\|\mathbf{B}$ become

$$\sigma_{\mathrm{eff}}/\sigma^*=[1\pm(p+2)jb/(2p+1)]/[1+b^2(p+1)/3p]. \tag{4}$$

Linear polarization for $\boldsymbol{\alpha}\perp\mathbf{B}$ yields

$$\sigma_{\mathrm{eff}}/\sigma^*=[1+3b^2/(2p+1)]/[1+(p+2)b^2/3p], \tag{5}$$

where $\sigma^*=ne^2/m^*(\nu+j\omega)$, $m^*=3m_1m_2/(2m_1+m_2)$, $p=m_1/m_2$, and $b=eB/m_2(\nu+j\omega)$, m_1, m_2 being the longitudinal and transverse components of the mass tensor, and ν the collision frequency, assumed independent of energy. The expressions for σ_{eff} with **B** along other principal directions are more involved except for the linear polarization, where for the eight ellipsoids, **B** along [111] and [110] directions, the conductivities become, respectively,

$$\frac{\sigma_{\mathrm{eff}}}{\sigma^*}=\frac{[1+(7p+2)b^2/3p(2p+1)]}{[1+(p+8)b^2/9p]}; \tag{6a}$$

$$\frac{\sigma_{\mathrm{eff}}}{\sigma^*}=\frac{[1+(p+2)b^2/(2p+1)]}{[1+(2p+1)b^2/3p]}. \tag{6b}$$

For the six ellipsoids with **B** along [110] and [001] axes, the conductivities become, respectively,

$$\frac{\sigma_{\mathrm{eff}}}{\sigma^*}=\frac{[1+(p+5)b^2/2(2p+1)]}{[1+(p+1)b^2/2p]}; \tag{7a}$$

$$\frac{\sigma_{\mathrm{eff}}}{\sigma^*}=1. \tag{7b}$$

Setting $\Gamma=0$ gives equations for plasma oscillation frequencies. These become real if ν is neglected, i.e., for "pure" samples, low temperatures, and high frequencies. $\mathbf{E}\|\mathbf{B}$ results in linear and $\mathbf{E}\perp\mathbf{B}$ in elliptical (or circular if $\sigma_{11}=\sigma_{22}$) polarization. The equations, identical for **B** along the [111] and [100] directions for the six and eight ellipsoid models respectively, are

$$\omega^4-\omega^2[(p+2)\omega_2^2/3p+\omega_p^2]+3\omega_p^2\omega_2^2/(2p+1)=0, \tag{8a}$$

$$\omega^3-\omega[(p+2)\omega_2^2/3p+\omega_p^2] \pm(p+2)\omega_p^2\omega_2/(2p+1)=0, \tag{8b}$$

where $\omega_p^2=ne^2/m^*\epsilon$ and $\omega_2=eB/m_2$.

Equations (8a) and (8b) describe the linear and circular polarizations respectively. With $\mathbf{E}\|\mathbf{B}$ and along the [100] axes, for six ellipsoids, there is no magnetic effect and $\omega^2=\omega_p^2$. Other cases will be discussed in a later publication.

The above results depend on crystal orientation and parameters related to energy surface curvature and may be utilized for investigating the shape of energy bands in anisotropic semiconductors at microwave frequencies. The approach outlined may also be applicable for analyzing the anisotropy of warped spheres.[3] Approximate expressions of the conductivity tensor for the latter are being derived from Boltzmann transport theory by Zeiger.[4] Actual experiments require finite samples and depolarizing effects may have to be taken into account as suggested by Kittel.[5] The conductivities would then contain components of a depolarizing tensor.

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[†] Now at Harvard University, Cambridge, Massachusetts.

[1] E. V. Appleton, U.R.S.I. Reports, Washington (1927).

[2] S. Meiboom and B. Abeles, Phys. Rev. **93**, 1121 (1954); Lax, Zeiger, Dexter, and Rosenblum, Phys. Rev. **93**, 1418 (1954); Dexter, Lax, Kip, and Dresselhaus, Phys. Rev. **96**, 222 (1954).

[3] Dexter, Zeiger, and Lax, Phys. Rev. **95**, 557 (1954); R. N. Dexter and B. Lax, Phys. Rev. **96**, 223 (1954).

[4] H. J. Zeiger (private communication).

[5] C. Kittel, Physica (to be published).

Space Charge Layer Near the Surface of a Ferroelectric

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It is known that a space charge layer can exist near the surface of solids. In the case of a *semiconductor*, this layer arises from the trapping of electrons in the surface traps.[1] The electric potential V between the surface and the bulk is about 1 volt, and the thickness of the layer is generally between 10^{-4} cm and 10^{-6} cm. Hence, electric fields of the order of magnitude 10^4 volts/cm to 10^6 volts/cm may prevail. In the case of an *ionic conductor*, the space charge layer is due to the fact that the surface is a source or a sink of vacancies.[2] V is again of the order of magnitude 1 volt. The thickness of the layer decreases with increasing vacancy concentration. Thin space charge layers ($<10^{-5}$ cm) require a vacancy concentration which exceeds 10^{17}

cm^{-3}. In *intrinsic* ionic conductors this concentration is generally reached only at rather elevated temperatures. In *extrinsic* ionic conductors, however, an impurity concentration near 10^{18} cm^{-3} leads to the formation of what we might call an "ionic Schottky exhaustion layer." Its thickness lies between 10^{-5} and 10^{-6} cm and does not depend sensitively upon the temperature.[3] Hence, fields as high as 10^5 volts/cm to 10^6 volts/cm may result.

An interesting effect should arise from these space charge layers in the case of highly polarizable crystals, such as ferroelectrics above the Curie point. Fields of 10^5 to 10^6 volts/cm induce the saturation polarization. The resulting piezoelectric or electrostrictive strain is about 1 percent and thus would be easily observable. [The fact that the thickness of the layer is proportional to $\sqrt{\epsilon}$, where ϵ is the static dielectric constant, should not prevent this effect: by inserting the dielectric constant of the saturated crystal ($\epsilon \approx 200$) one obtains a layer which is still thin enough to justify the assumption of dielectric saturation.] To summarize, we can say that a ferroelectric semiconductor or a ferroelectric extrinsic ionic conductor can exhibit a surface layer of a thickness between 10^{-5} cm and 10^{-6} cm where saturation polarization and the corresponding piezoelectric strain prevails. This layer does not depolarize if the crystal is heated above the Curie temperature of the bulk because the properties of the space charge layer do not depend sensitivity upon the temperature as long as the conditions for dielectric saturation are fulfilled.

There is considerable experimental evidence that such a layer exists in the case of ferroelectric $BaTiO_3$ which is known to be a semiconductor[4] and which might also be an extrinsic ionic conductor to some extent. Diffusion measurements indicate that intrinsic ionic conduction is negligible in the temperature range which is of interest here.[5] X-ray and electron diffraction experiments with very small $BaTiO_3$ particles have led to the following conclusions[6]:

1. There is a discrepancy in symmetry between a surface layer of a thickness of about 100 A and the bulk. The misfit between the surface layer and the bulk is smaller below the Curie temperature of the bulk. Thus the structure of the surface layer is closer to the tetragonal structure of the polarized lattice than to the cubic structure of the unpolarized lattice.

2. Electron diffraction experiments indicate a tetragonal strain in the surface layer which is slightly larger than the tetragonal strain of the bulk below the Curie temperature. The tetragonal surface strain does not vanish if the crystal is heated above the Curie temperature of the bulk.

It is interesting to note that in the case of ferroelectric KH_2PO_4 no evidence for a polarized surface layer was found.[7] As KH_2PO_4 is not a semiconductor and generally much purer than $BaTiO_3$, this supports the view that the observed surface strain in the case of $BaTiO_3$ is due to an ionic or electronic space charge layer. This layer may also account for the observation that very thin, virgin $BaTiO_3$ crystals do not show normal dielectric hysteresis at low voltages V, though the apparent electric field (calculated as V/d, where d is the thickness of the crystal) is larger than the coercive field. The space charge layer has to be broken down before the normal dielectric hysteresis can be observed.[8]

The author is indebted to J. Bardeen, R. J. Maurer, and F. Seitz, for illuminating discussions.

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[1] John Bardeen, Phys. Rev. **71**, 717 (1947).

[2] J. Frenkel, *Kinetic Theory of Liquids* (Clarendon Press, Oxford, 1947).

[3] K. Lehovec, J. Chem. Phys. **21**, 1223 (1953).

[4] Busch, Flury, and Merz, Helv. Phys. Acta **21**, 212 (1948); S. Nomura and S. Sawada, J. Phys. Soc. Japan **5**, 227 (1950); E. K. Weise and J. A. Lesk, J. Chem. Phys. **21**, 801 (1953).

[5] A. Garcia-Verduch and R. Lindner, Ark. Kemi **5**, 313 (1953).

[6] Anliker, Brugger, and Känzig, Helv. Phys. Acta **27**, 99 (1954).

[7] Jaccard, Känzig, and Peter, Helv. Phys. Acta **26**, 521 (1953).

[8] W. J. Merz, Phys. Rev. **76**, 1221 (1949).

Diamagnetic Resonance in Electronic Conductors

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In a recent Letter with the above title,[1] Dorfman points out that he had published an article in 1951 predicting the general features of diamagnetic ("cyclotron") resonance in electronic conductors, which would therefore be prior to my detailed theoretical treatment[2] appearing in 1952.

In order to avoid any possible misunderstandings, I should like to draw attention to the fact that I had described the effect at the 1951 International Conference on Very Low Temperatures, and (like Dorfman) had emphasized that it would lead to a direct estimate of the effective mass of the carriers. The publications of such general descriptions by myself[3] and Dorfman[4] were therefore independent and essentially simultaneous. The detailed treatment[2] appearing in the *Proceedings of the Royal Society* (*London*) for 1952 was taken from my 1951 doctorate thesis.[5]

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[1] J. G. Dorfman, Phys. Rev. **96**, 1704 (1954).

[2] R. B. Dingle, Proc. Roy. Soc. (London) **A212**, 38 (1952).

[3] R. B. Dingle, Proceedings of the International Conference on Very Low Temperatures, edited by R. Bowers (Oxford, 1951), abstract on p. 165.

[4] J. G. Dorfman, Doklady Akad. Nauk. S.S.S.R. **81**, 765 (1951). (Unfortunately, this volume does not appear to have become available in England until after the publication of my 1952 paper.)

[5] R. B. Dingle, doctorate thesis, Cambridge University (1951), Chap. VI.