

or the charge carriers created by the incident radiation form avalanches of prebreakdown magnitudes and excitation by impact of a number of activators per incident photon is attained. The charge carrier multiplication is attainable with the high fields characteristic of electronic breakdown. Rupture may be avoided by the high-field region being sufficiently thin so that the required number of multiplications for breakdown cannot occur.

The alternative electroluminescent mechanism of minority charge carrier injection followed by capture by appropriate activator systems also conceptually provides a method of radiation amplification in a phosphor.² In this case, the photons create charge carriers which are trapped, thereby yielding a space charge facilitating the transport of carriers of opposite sign which are subsequently captured by the activator systems resulting in ionization. Capture of the majority charge carrier then leads to photon emission, conceivably in greater quantity than the initial photon absorption.

The observations of Cusano³ on thin films of ZnS:Mn,Cl are in accord with the impact excitation mechanism of radiation amplification. The energy levels of the Mn activator system are deep-lying, below the valence band of ZnS, and therefore, collision excitation rather than the capture of injected charge carriers must be involved. ZnS:Mn,Cl, in contrast with electroluminescent ZnS:Cu, is relatively free of deep donors. The Cl coactivator introduces electron traps approximately 0.3 eV below the conduction band. The absorption of 3650 Å radiation apparently excites valence electrons to these states and the coactivator can thus behave as a donor in a high-field region. The rectification of the light-amplifying phosphor film is not unexpected. The Piper-Williams theory¹ emphasized that a cathode barrier, probably of the exhaustion type, exists at the metal-semiconductor contact for electroluminescent ZnS:Cu single crystals. A similar barrier probably exists at the metal-semiconductor contact of the ZnS:Mn,Cl films; and electroluminescence, initiated by 3650 Å radiation, occurs only when the metal electrode is negative. The conditions at the ZnS—TiO₂ interface are less apparent. Although the average field through the film during light amplification is 10⁵ v/cm, the field in the cathode barrier is probably 10⁶ v/cm. In fact, the 100 Å shift in the emission spectrum observed under these conditions of excitation can be accounted for by a field of this magnitude perturbing the Mn activator system essentially by the Stark effect. Fields of 10⁵ to 10⁶ v/cm are also indicative of the collision excitation mechanism of electroluminescence.

¹ W. W. Piper and F. E. Williams, *Phys. Rev.* **87**, 151 (1952); *Brit. J. Appl. Phys.*, Supplement No. 4, 39 (1955).

² W. W. Piper and F. E. Williams, *Phys. Rev.* (to be published).

³ D. A. Cusano, *Bull. Am. Phys. Soc.* **30**, No. 1, 30 (1955); and preceding Letter [*Phys. Rev.* **98**, 546 (1955)].

Anomaly in the Low-Temperature Atomic Heat of Silver*

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SINCE the publication of an earlier Letter¹ with this title, Clement,² analyzing the effect of deviations of earlier temperature scales from the 48 scale, pointed out that deviations of the adopted scale from the true thermodynamic scale may cause apparently significant anomalies in calorimetric results. The recent work of Erickson and Roberts³ and of Keller³ substantiate the deductions of Kistemaker³ concerning deviations from the 48 scale, and a new scale, for convenience called the 55 scale, seems to be established. We recalculated the specific heat data based on the adopted 48 scale, using the formula

$$c_{55} = c_{48} [1 + d(T_{48} - T_{55})/dT].$$

In plotting c_{48}/T versus T^2 , it was not possible to draw one straight line through the data and an anomaly appeared significant. However, this anomaly disappears if the 55 scale is used and one straight line is able to represent the data within their accuracy. Using least squares, we now obtain for the atomic heat of silver below 4°K: $c = 0.66T + 0.170T^3$ millijoules/mole deg, which corresponds to a Debye parameter θ_0 of 225°K.

* Assisted by Signal Corps.

¹ P. H. Keesom and N. Pearlman, *Phys. Rev.* **88**, 140 (1952).

² J. R. Clement, *Phys. Rev.* **93**, 1420 (1954).

³ See W. E. Keller, *Phys. Rev.* **97**, 1 (1955).

Propagation and Plasma Oscillation in Semiconductors with Magnetic Fields*

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MAGNETO-IONIC theory¹ can be extended to semiconductors whose energy surfaces in the Brillouin zone are ellipsoidal² or warped spheres³ possessing cubic symmetry. With a magnetic field **B** along the [001], [110], or [111] axes, the rf conductivity tensors for electrons in germanium and silicon can be written

$$\sigma = \begin{pmatrix} \sigma_{11} & \sigma_{12} & 0 \\ -\sigma_{12} & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}, \quad (1)$$

where the z axis is along **B**. For the [001] and [111] directions $\sigma_{11} = \sigma_{22}$. The conductivity tensors, obtained for each of the eight or six ellipsoids in their respective

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

$$\Gamma^2 = -\omega^2 \epsilon \mu_0 + j \omega \mu_0 \sigma_{\text{eff}}, \quad (2)$$

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

$$\alpha \parallel \mathbf{B}: \quad \sigma_{\text{eff}} = \frac{1}{2}(\sigma_{11} + \sigma_{22}) \pm j \left[\sigma_{12}^2 - \frac{1}{4}(\sigma_{11} - \sigma_{22})^2 \right]^{1/2}, \quad (3a)$$

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

$$\sigma_{\text{eff}} = \frac{\omega \epsilon (\alpha_2^2 \sigma_{11} + \alpha_1^2 \sigma_{22}) - j(\sigma_{12}^2 + \sigma_{11} \sigma_{22})}{\omega \epsilon - j(\alpha_1^2 \sigma_{11} + \alpha_2^2 \sigma_{22})}, \quad (3c)$$

where α is the unit vector along Γ . For longitudinal propagation, Eq. (3a), \mathbf{E} is elliptically polarized normal to \mathbf{B} and circularly polarized when $\sigma_{11} = \sigma_{22}$. Transverse propagation has two cases, (3a) corresponding to linear polarization with \mathbf{E} along \mathbf{B} and (3b) to elliptical polarization with $\mathbf{E} \perp \mathbf{B}$. The effective conductivities for \mathbf{B} along the [001] direction for the eight and the [111] for the six ellipsoids are identical, and for $\alpha \parallel \mathbf{B}$ become $\sigma_{\text{eff}}/\sigma^* = [1 \pm (p+2)jb/(2p+1)]/[1 + b^2(p+1)/3p]$. (4)

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

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

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 \mathbf{B} along other principal directions are more involved except for the linear polarization, where for the eight ellipsoids, \mathbf{B} along [111] and [110] directions, the conductivities become, respectively,

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

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

For the six ellipsoids with \mathbf{B} along [110] and [001] axes, the conductivities become, respectively,

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

$$\frac{\sigma_{\text{eff}}}{\sigma^*} = 1. \quad (7b)$$

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. $\mathbf{E} \parallel \mathbf{B}$ results in linear and $\mathbf{E} \perp \mathbf{B}$ in elliptical (or circular if $\sigma_{11} = \sigma_{22}$) polarization. The equations, identical for \mathbf{B} along the [111] and [100] directions for the six and

eight ellipsoid models respectively, are

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

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

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 $\mathbf{E} \parallel \mathbf{B}$ 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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¹ E. V. Appleton, U.R.S.I. Reports, Washington (1927).

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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}