

host was based on only the room temperature value of λ_{111} in $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$ because the crystal-field calculation was not consistent with the experimental data available for small cobalt concentrations.¹ Finally, it should be remarked that the values of E_t , V_e , and V_s of both hosts may be raised or lowered by a common factor (say 40%) without impairing seriously agreement with experiment. The main reason for this is that the value of V_e is not fixed well by the tetragonal distortion of CoO because of some uncertainty in the wave function (Kanamori's factor $a^2+c^2-2b^2$) and because of the lack of assurance that V_e should be the same in CoO as in cobalt-substituted ferrites.

Further work is suggested by the observation that anisotropy and magnetostriction of cobalt-substituted magnetite and cobalt-substituted manganese ferrite are consistent with the orbital doublet model of the Co^{2+} ion. It would be worthwhile to carry out further experiments at low temperatures where the highly specific effects of the cobalt ion would be more striking. At absolute zero one should expect nearly discontinuous curves of torque versus angle¹⁴ and radically non-sinusoidal strain-vs-angle curves which are calculable from our work. The manganese ferrite host is perhaps the better choice for such experiments because the agreement at higher temperatures is better and because

¹⁴ J. Smit, F. K. Lotgering, and U. Enz, *J. Appl. Phys., Suppl.* to Vol. 31, 137S (1960).

it has no structural complications such as the orthorhombic transition¹⁵ occurring at 120°K in magnetite.¹⁶

The manganese-ferrite host has the disadvantage of a partially inverse (20%) structure, which means that there is a largely disordered distribution of divalent and trivalent cations on both octahedral and tetrahedral sites. This means that some unsymmetric random crystal field may act on the cobalt ion and complicate its magnetic properties. In magnetite there is also a mixture of divalent and trivalent iron on octahedral sites. This distribution, however, becomes ordered¹⁵ in the orthorhombic phase. If the crystal field due to the ordering has an appreciable effect on the state of the cobalt ion, then low temperature studies of cobalt-substituted magnetite would provide valuable information about magnetite itself as well as about the specific effects of the cobalt ion.

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¹⁵ E. J. Verwey, P. W. Haayman, and F. C. Romeijn, *J. Chem. Phys.* **15**, 181 (1947); W. C. Hamilton, *Phys. Rev.* **110**, 1050 (1958).

¹⁶ However, preliminary microwave measurements by R. W. Teale (private communication) and torque measurements by R. F. Pearson (private communication) indicate that the anisotropy of $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ at low temperatures does not agree well with the theory of references 2 and 3.

Behavior of Hot Electrons in Microwave Fields

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A strong external electric field in a semiconductor produces hot electrons. In the present paper, we investigate theoretically the currents produced by such electrons in a microwave field. We discuss two special cases: Case A deals with a strong steady electric field on which a weak microwave field of frequency ω is superimposed. It is found that in addition to a steady current there is an alternating current of frequency ω which leads the microwave field by a phase given by Eq. (30). The phase difference is negligible at low frequency, but becomes appreciable at frequencies $\omega \approx (1/\tau_0)(1/100)$, at liquid-nitrogen temperature. Here τ_0 is the electron-phonon relaxation time of thermal electrons. (Interaction with acoustic modes only is considered.) In case B, we consider the effect of a strong microwave field by itself. Here the current has a strong component of frequency ω and a weaker component of frequency 3ω . We find phases similar to those in case A. Results for case B are valid if $1/\tau_0 > \omega > (1/\tau_0)(1/100)$ at liquid-nitrogen temperature.

1. INTRODUCTION

THE purpose of the present paper is to investigate theoretically the currents introduced by an alternating field in a nonpolar semiconductor when the current carriers have average energy per particle appreciably larger than that of the lattice.

The idea of hot carriers was first introduced by

Fröhlich¹ in connection with the theory of dielectric breakdown. In the presence of an external electric field F , the free electrons (or holes) in a semiconductor continuously gain energy from the field. In a steady state, they must lose it to the lattice at the same average rate as they gain it. Since the rate of loss of

¹ H. Fröhlich, *Proc. Roy. Soc. (London)* **A188**, 521 (1947).

energy from electrons to lattice increases with increasing electronic energy, one expects that in a steady state the mean electronic energy \bar{E} will be higher than its mean energy $\frac{3}{2}kT_0$ in the absence of an electric field. (Here T_0 is the temperature of the lattice.) The electrons can reach their own thermal equilibrium if they exchange energy among themselves faster than with the lattice. A thermal equilibrium among electrons permits one to treat electrons collectively with an electronic temperature $T = \frac{2}{3}(\bar{E}/k)$. Fröhlich and Paranjape² have estimated the rate of loss of energy of a fast electron to the other electrons through Coulomb interaction; and compared it with the rate of loss of its energy to the lattice vibrations. The former rate is proportional to n the density of electrons, and the latter is independent of n . A critical density of electrons is thus necessary to make the energy exchange amongst electrons the faster process. It is found that densities of order $10^{14}/\text{cm}^3$ are adequate to describe the electrons by a temperature $T > T_0$.

Even if the electronic density is so low that they cannot reach thermal equilibrium, \bar{E} is always higher than $\frac{3}{2}kT_0$. It follows from Stratton's calculations³ that in this case \bar{E} differs from $\frac{3}{2}kT$ only by a numerical factor of order unity.

In the present paper, we neglect factors of order unity. We treat all electrons as having the same energy kT , and assume that they interact with the acoustic modes of lattice vibrations (i.e., we neglect interaction with the optical modes).

The present problem, even with the above simplifications, becomes quite unmanageable to solve exactly. We need to estimate first the electronic temperature as a function of time t . In the presence of a purely sinusoidal electric field of low frequency, the electronic temperature will follow the field adiabatically; i.e., at every instant, the electronic temperature will assume a value that can be associated with a steady field at that instant. Since T is not a simple function of F for all values of F , $T(t)$ would be rather a complicated function to handle. If the maximum value of T is much greater than T_0 , the function $T(t)$ would be very unsymmetrical about the mean value \bar{T} of $T(t)$. On the other hand, if we consider a field of very high frequency, then T would not be able to follow the field adiabatically. It has already been pointed out by Fröhlich and Paranjape² that it takes many collisions for hot electrons to lose their excess energy. If we associate a time constant $\bar{\tau}$ with the rise or decay time of the electronic temperature, then at high frequencies $\omega > 1/\bar{\tau}$. At these high frequencies, the electronic temperature would be expected to oscillate nearly symmetrically about its mean value. It would then be possible to develop $T(t)$ in Fourier series in 2ω , and retain only \bar{T} and the first time-dependent term.

2. CALCULATION

The method of calculating the electronic temperature in time-dependent electric fields is similar to that given by Fröhlich¹ who has considered the problem of constant fields. In a steady field, Fröhlich equates the rate of transfer of energy from the electric field to the electrons, $(\partial E/\partial t)_F$, to that from electrons to lattice vibrations, $(\partial E/\partial t)_L$.

In the present problem, since the electric field is a function of time, we have

$$(\partial E/\partial t)_F - (\partial E/\partial t)_L = \partial E/\partial t. \quad (1)$$

That is, the difference of the two quantities on the left-hand side of Eq. (1) gives us the rate of change of energy $\partial E/\partial t$ of the electrons.

Let $\tau(T, T_0) \equiv \tau$ denote the time of relaxation of an electron of energy kT interacting with lattice vibrations at a temperature T_0 . It is well known that τ decreases as T increases, if $T \gg T_0$, then $\tau \ll \tau_0$, where $\tau_0 \equiv \tau(T_0, T_0)$ is the time of relaxation obtained from low-field mobilities. In the present problem, we need $T(t)$ to calculate $j(t)$ for a given $F(t)$.

Let the electric field be given by

$$F(t) = F_0 + F_1 \sin \omega t, \quad (2)$$

and assume throughout that $\omega \tau_0 \ll 1$, so that the conductivity can be replaced by its static value $\sigma = e^2 \tau / m$. Therefore $j(t) = \sigma F$ is the electric current and hence,

$$(\partial E/\partial t)_F = j(t)F(t) = (e^2 \tau / m)(F_0 + F_1 \sin \omega t)^2. \quad (3)$$

Here m is the effective mass of electrons which we take as constant.

Calculation of $(\partial E/\partial t)_L$ has been carried out by several authors.^{2,3} A simple derivation of their results can be given if T is sufficiently larger than T_0 , i.e., for sufficiently strong fields F .

Conservation of energy and momentum lead at once to the conclusion that the average exchange of energy per collision between the lattice and an electron is roughly $(kTms^2)^{\frac{1}{2}}$, where s is the velocity of sound. Since the probability of absorption or emission of a lattice quantum is proportional to \bar{n} or $\bar{n}+1$, respectively, the net loss of energy $(kTms^2)^{\frac{1}{2}}$ by an electron requires $2\bar{n}+1$ collisions with the lattice. Here \bar{n} is the average number of phonons which can interact with an electron of energy kT .

$$\bar{n} = \{\exp[(kTms^2)^{\frac{1}{2}}/kT_0] - 1\}^{-1} \approx kT_0/(kTms^2)^{\frac{1}{2}}, \quad (4)$$

provided

$$(kTms^2)^{\frac{1}{2}}/kT_0 < 1. \quad (5)$$

The above approximation⁴ holds for electric fields in the range in which the mobility is found proportional to $F^{-0.5}$. It thus follows that

$$(\partial E/\partial t)_L = (kTms^2)^{\frac{1}{2}}/(\tau \times 2\bar{n}). \quad (6)$$

² H. Fröhlich and B. V. Paranjape, Proc. Phys. Soc. (London) **B69**, 21 (1956).

³ R. Stratton, Proc. Royal Soc. (London) **A242**, 355 (1957).

⁴ B. V. Paranjape, Proc. Phys. Soc. (London) **B70**, 628 (1957).

Following the usual derivation⁵ of τ , one finds

$$\frac{1}{\tau} = \frac{1}{\tau_0} \frac{kT(ms^2)^{\frac{1}{2}}}{(kT_0)^{\frac{1}{2}}} \bar{n} \approx \frac{1}{\tau_0} \left(\frac{T}{T_0} \right)^{\frac{1}{2}}, \quad (7)$$

which for $T = T_0$ leads to $\tau = \tau_0$ as required.

Thus Eq. (1), using Eqs. (2) to (7), yields

$$\begin{aligned} \frac{e^2 \tau_0}{m} (F_0 + F_1 \sin \omega t)^2 \left(\frac{T_0}{T} \right)^{\frac{1}{2}} - \left(\frac{T}{T_0} \right)^{\frac{1}{2}} \frac{ms^2}{2\tau_0} \\ = kT_0 \frac{\partial(T/T_0)}{\partial t}. \end{aligned} \quad (8)$$

It should be noted that Eq. (8) holds rigorously only if T is sufficiently larger than T_0 . This should always hold for high frequency fields of sufficient magnitude, but not necessarily for low frequencies.

Special Cases

Case A

We first consider

$$F(t) = F_0 + F_1 \sin \omega t, \quad (9)$$

$$F_1/F_0 = \lambda \ll 1. \quad (10)$$

Define

$$a_A^2 = 2e^2 \tau_0^2 F_0^2 / m^2 s^2, \quad (11)$$

$$(T/T_0) = y, \quad (12)$$

$$2(kT_0/ms^2)\tau_0 = \bar{\tau}, \quad (13)$$

$$t/\bar{\tau} = t'. \quad (14)$$

Thus, Eq. (8) becomes

$$a_A^2 (1 + \lambda \sin \omega t')^2 = y^2 + y^{\frac{1}{2}} \dot{y}. \quad (15)$$

The dot indicates the derivative with respect to t' . Since λ is small we expect the solution of the form

$$y = y_0 + \lambda y_1 + \lambda^2 y_2 + \dots \quad (16)$$

Equating the coefficients of λ^n we have for the coefficient of the term independent of λ

$$a_A^2 = y_0^2 + y_0^{\frac{1}{2}} \dot{y}_0. \quad (17)$$

Solution of (17) for sufficiently long t' gives

$$y_0 = a_A, \quad \text{i.e.,} \quad \dot{y}_0 = 0. \quad (18)$$

The coefficient of λ requires

$$2a_A^2 \sin \omega \bar{\tau} t' = 2y_0 y_1 + y_0^{\frac{1}{2}} \dot{y}_1, \quad (19)$$

so that

$$y_1 = \frac{a_A}{[1 + (\omega \bar{\tau})^2 / 4a_A]} \left[\sin \omega t' - \frac{\omega \bar{\tau}}{2(a_A)^{\frac{1}{2}}} \cos \omega t' \right].$$

Thus, up to first order in λ

$$\begin{aligned} y &= a_A \left[1 + \lambda \frac{\sin \omega t' - [\omega \bar{\tau} / 2(a_A)^{\frac{1}{2}}] \cos \omega t'}{1 + (\omega \bar{\tau})^2 / 4a_A} \right] \\ &= a_A [1 + \lambda \cos \varphi_A \sin(\omega t' - \varphi_A)], \end{aligned}$$

where

$$\tan \varphi_A = \omega \bar{\tau} / (2a_A)^{\frac{1}{2}}.$$

Case B

Let F_0 be zero and F_1 sufficiently large so that Eq. (8) still holds. We then have

$$a_B^2 (1 - \cos 2\omega t') = y^2 + y^{\frac{1}{2}} \dot{y}, \quad (20)$$

where

$$a_B = e\tau_0 F_1 / ms. \quad (21)$$

As mentioned in the introduction, let ω be sufficiently high so that we can expect the temperature T to oscillate sinusoidally with frequency 2ω and with a relatively small amplitude around a mean value. We then expect the solution of Eq. (20) to be of the form

$$y = y_0 + y_1 + \dots, \quad (22)$$

where y_0 is assumed time independent and y_1 is periodic with frequency 2ω . We further assume $|y_1| \ll y_0$.

Substituting Eq. (22) into Eq. (20), we find for the time-independent part

$$y_0 = a_B. \quad (23)$$

To the lowest order in y_1 , then

$$-a_B^2 \cos 2\omega \bar{\tau} t' = 2y_0 y_1 + y_0^{\frac{1}{2}} \dot{y}_1, \quad (24)$$

so that using Eq. (14)

$$\begin{aligned} y_1 &= -\frac{1}{2} a_B \frac{\cos 2\omega t' + (\omega \bar{\tau} / a_B^{\frac{1}{2}}) \sin 2\omega t'}{1 + (\omega \bar{\tau})^2 / a_B} \\ &= -\frac{1}{2} a_B \cos \varphi_B \cos(2\omega t' - \varphi_B), \end{aligned} \quad (25)$$

where

$$\tan \varphi_B = \omega \bar{\tau} / a_B^{\frac{1}{2}}.$$

Hence, up to first order in y_1 , the complete solution of (20) is

$$y = a_B [1 - \frac{1}{2} \cos \varphi_B \cos(2\omega t' - \varphi_B)]. \quad (26)$$

Using Eqs. (4), (7), and (12), it now follows that the current is given in general by

$$j(t) = \frac{e^2 \tau F(t)}{m} = \frac{e^2 \tau_0 F(t)}{m} y^{-\frac{1}{2}}. \quad (27)$$

In our two cases, then, remembering that y_1 is always assumed small compared with y_0 , we have in case A up to order λ [external field $F_0(1 + \lambda \sin \omega t)$],

$$\begin{aligned} j_A(t) &= \frac{e^2 \tau_0}{m} \frac{F_0}{(a_A)^{\frac{1}{2}}} \\ &\times [1 + \lambda \{ \sin \omega t - \frac{1}{2} \cos \varphi_A \sin(\omega t - \varphi_A) \}], \end{aligned} \quad (28)$$

⁵ A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1954), 2nd ed.

which is of the form

$$j_A(t) = \frac{e^2 \tau_0}{m} \frac{F_0}{(a_A)^{\frac{1}{2}}} [1 + \lambda' \sin(\omega t + \eta)], \quad (29)$$

where

$$\tan \eta = \frac{\frac{1}{2} \cos \varphi_A \sin \varphi_A}{1 - \frac{1}{2} \cos^2 \varphi_A}, \quad (30)$$

and

$$\lambda' = \lambda \left\{ \left(1 - \frac{1}{2} \cos^2 \varphi_A\right)^2 + \frac{1}{4} \cos^2 \varphi_A \sin^2 \varphi_A \right\}^{\frac{1}{2}}; \quad (31)$$

and in case B,

$$j_B(t) = \frac{e^2 \tau_0}{m} \frac{F_1}{a_B^{\frac{1}{2}}} \sin \omega t \left[1 + \frac{1}{4} \cos \varphi_B \cos(2\omega t - \varphi_B) \right], \quad (32)$$

which is of the form

$$j_B(t) = \frac{e^2 \tau_0}{m} \frac{F_1}{a_B^{\frac{1}{2}}} [\gamma_1 \sin(\omega t + \delta_1) + \gamma_2 \sin(3\omega t + \delta_2)], \quad (33)$$

where

$$\gamma_1 = \left\{ \left(1 - \frac{1}{8} \cos^2 \varphi_B\right)^2 + \left(\frac{1}{8} \sin \varphi_B \cos \varphi_B\right)^2 \right\}^{\frac{1}{2}}, \quad (34)$$

$$\tan \delta_1 = \frac{\frac{1}{8} \sin \varphi_B \cos \varphi_B}{1 - \frac{1}{8} \cos^2 \varphi_B}, \quad (35)$$

$$\gamma_2 = \frac{1}{8} \cos \varphi_B, \quad \text{and} \quad \delta_2 = -\varphi_B. \quad (36)$$

3. DISCUSSION

The above results are derived on the assumption that $\omega \tau_0 \ll 1$. This upper limit on ω holds up to quite high frequencies, since τ_0 (the relaxation time obtained from low-field mobilities) at liquid-nitrogen temperature is of the order of 10^{-12} sec. There is no lower limit on the frequency in case A, since it is assumed here that the periodic part of the field is very small compared with the steady field.

We notice that in case A the current has a term independent of time in zeroth order and a term of the imposed frequency ω in first order with a phase shift η .

In case B, on the other hand, we obtain in Eq. (33) a current which has one term with frequency ω and another term with frequency 3ω . Of course, a contribution to the 3ω frequency term would have been obtained if we had continued the development of y to include terms with period 4ω . These terms are of smaller order and therefore can be neglected provided $\omega \tau$ is large.

From the structure of our differential equation it

can be expected that our method certainly converges for case B if $\omega \tau > a_B^{\frac{1}{2}}$, i.e., from Eqs. (13) and (21),

$$\omega \tau_0 > \frac{ms^2}{2kT_0} \left(\frac{e\tau_0 F_1}{ms} \right)^{\frac{1}{2}}. \quad (37)$$

It might well be, however, that our solution is reasonably good even at lower frequencies. We note in this connection that since deviations from Ohm's law occur when $(e\tau_0 F_1/ms) \approx 1$, Eq. (37) requires $\omega \tau_0 > 1/100$ at 78°K (assuming $ms^2 \approx 1^\circ\text{K}$). Thus, an $\omega \tau_0$ satisfying Eq. (37) can also satisfy the condition $\omega \tau_0 \ll 1$.

The interesting feature of this experiment is that application of a strong high-frequency field leads, in view of the periodic behavior of electronic temperature, to a current which besides having a strong component with frequency ω and a phase shift δ_1 has a weaker component of frequency 3ω . Equation (35) shows that the phase shift becomes appreciable at frequencies much below those in which it would occur in weak fields. The 3ω component is a direct consequence of the behavior of the electron temperature: T has a time-independent term and a term of frequency 2ω . Measurement of the current in strong high-frequency fields would enable us to confirm general features of our model. It also would permit direct measurement of $(\omega \tau/a_B^{\frac{1}{2}})$. a_B according to Eq. (21) is known in terms of τ_0 and m which can be measured at weak fields. Appropriate measurements in strong high-frequency fields, therefore, would permit experimental determination of τ , which is a measure of the time required for hot electrons to cool down.

These conclusions were reached on the basis of our model which takes account of interaction of electrons with acoustic modes only, but neglects interaction with optical modes. The proposed experiment would, therefore, be able to test whether or not strong deviations from this model must be contemplated.

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