sulfate signal was approximately 20 times the height of the sodium signal. On the basis of a $1/T$ dependence of the susceptibility of the copper sulfate, the signal from it should increase by about a factor of 4 in going from 300°K to 77°K. This means that the signal from the sodium decreased by about a factor of 5 in going to the lower temperature. A major fraction of this decrease is perhaps to be attributed to the decrease in skin depth at the lower temperature, owing to the lower resistance of Na. The remainder of the change may be due to changes in the width of the absorption curves. It seems clear from these results that the observed line is not caused by a paramagnetic impurity in the specimen.

We believe that the dominant mechanism of line broadening in the specimen may be the random phase and frequency modulation of the microwave field as seen by an observer on a conduction electron diffusing around in the eddy current field of the metal. Spin-spin and spin-lattice relaxation times for conduction electrons in sodium have been calculated in detail by Overhauser.[4] His shortest relaxation time gives a line width less than one oersted. Yafet's calculated variation of g with the direction of the electronic wave vector gives a width of about one oersted. A rough estimate of the width arising from the diffusion mechanism[5] gives

$$\Delta H/H \approx N r_0 \Lambda^2, \tag{1}$$

where N is the concentration of conduction electrons, r_0 the classical radius of the electron, and Λ the electronic mean free path. This relation applies when Λ is much smaller than the skin depth and when the particle size is of the order of the skin depth or larger. The observed width is compatible with Λ of the order of 200A, whereas Λ from the conductivity of bulk sodium is about 3 times larger. The discrepancy may be caused by (a) the influence of very fine particles; (b) the rough approximations made in deriving Eq. (1); or (c) major structural distortions of the sodium lattice in the fine particles resulting from their production by supersonic fragmentation. One would expect to be able to sharpen the line by going to particle diameters (or film thicknesses) less the mean free path.

We wish to express our thanks to Mr. Frank Abell, who provided us with the finely divided sodium sample used in this experiment. This work was supported in part by the ONR.

[1] An account of this work was given by A. F. Kip at the ONR Conference on Magnetism, College Park, Maryland, Sept. 2–6, 1952, unpublished.
[2] W. A. Yager, Phys. Rev. 75, 316 (1949).
[3] Y. Yafet, Phys. Rev. 85, 478 (1952); Thesis, University of California, Berkeley, 1952, unpublished.
[4] A. W. Overhauser, Thesis, University of California, Berkeley, 1951, unpublished; Phys. Rev. (to be published).
[5] Detailed calculations are presently being carried out by Dr. Elihu Abrahams.

Interpretation of the Electron-Inertia Experiment for Metals with Positive Hall Coefficients

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I N a recent paper Brown and Barnett[1] described measurements of e/m for the conduction electrons of metals such as Mo and Zn which are known to have positive Hall effects. While their experimental results appear to be correct, I find it impossible to accept their conclusion that positive Hall effects cannot be explained by hole conduction in a nearly filled Brillouin zone as originally proposed by Peierls.[2] If this conclusion is correct, then a substantial part of the modern theory of solids would appear to need revision. It should also be pointed out that the Hall effect in nickel is negative[3] and not positive as stated by Brown and Barnett in reference 1.

The value of e/m obtained for conduction electrons in metals in an "electron-inertia" experiment should always be very nearly equal to the value for free electrons in slow motion, even if the conductor has a positive Hall effect. Darwin[4] has explained why the electron-inertia experiments do not reveal the energy levels in metals and lead to the ordinary value of e/m. Brown and Barnett imply that this contradicts the usual explanation of positive Hall effect based on hole conduction. In the opinion of the author of this letter, this is not the case.

Let us consider a specific representation of a metal, namely, a simple cubic lattice which, from the approximation of tight binding, has the following energy levels in the first Brillouin zone:[5]

$$E = E_0 - \alpha - 2\gamma \ (\cos k_x a + \cos k_y a + \cos k_z a), \tag{1}$$

where E is the electron energy, $\mathbf{k}$ is the electron wave vector; $-\pi/a \le k_x \le \pi/a$, etc., in the first zone. E_0, α, and γ are constants and a is the lattice parameter. In the neighborhood of the zone boundary ($k_x \cong \pm \pi/a$, etc.), the energy levels are to a good approximation given by

$$\epsilon = \epsilon_{\max} - (\hbar^2/2m^*)|\mathbf{l}|^2, \tag{2}$$

where $\epsilon = E - E_{\min}$, $E_{\min} = E_0 - \alpha - 6\gamma$, $\epsilon_{\max} = 12\gamma$, and $\hbar^2/2m^* = \gamma a^2$. $\mathbf{l}$ is a new wave vector which is related to $\mathbf{k}$ by the equations, $l_x = \pm \pi/a - k_x$, etc. Consider the case of a nearly filled zone with N_h unoccupied states or "holes," where the energy levels in the neighborhood of the Fermi level are given by Eq. (2). It is well known that the calculated Hall effect for this representation of a metal is positive with a Hall coefficient $R = 1/N_h e c$.[5]

Electric current density j_x is defined by the equation[6]

$$j_x = -e\Sigma_o v_x = +e\Sigma_u v_x, \tag{3}$$

where the summation index "o" indicates that the sum is to be taken over all occupied states and the index "u" indicates that the sum is to be taken over all unoccupied states. v_x is the average value of the velocity operator $(\hbar/im)(\partial/\partial x)$ which for electron wave functions of the Bloch type has the value[5]

$$v_x = (1/\hbar)(\partial \epsilon/\partial k_x). \tag{4}$$

There are two alternate expressions for the current by virtue of the fact that the sum over all states,

$$\Sigma_o v_x + \Sigma_u v_x = 0, \tag{5}$$

because there can be no current in a filled zone. When a simple expression such as Eq. (2) is available for the unoccupied energy levels near the zone boundary, it is convenient to carry out the summation over the unoccupied states and attribute the current to holes with a positive charge. However, it is not difficult to arrive at incorrect results by taking this interpretation too literally.

The momentum operator is $p_x = (\hbar/i)(\partial/\partial x)$, so that the total x component of momentum of the conduction electrons is simply

$$P_x = m\Sigma_o v_x = -(m/e)j_x, \tag{6}$$

making use of Eq. (3). Equation (6) is perfectly general and applies to either hole or electron conduction. The momentum of the conduction electrons is always in the opposite direction to the current. To be sure, the results of Brown and Barnett "discriminate against theories for which current and momentum can have the same direction," if the momentum is interpreted as that of the conduction electrons. They are in agreement with a common direction of the current and the momentum of holes. [The momentum of the holes is $\Sigma_u v_x = +(m/e)j_x$, making use of Eqs. (5) and (6).

The ordinary value of e/m appears in Eq. (6) so that any experiment such as the experiment in question, which is based on the relation between current and momentum, will measure the ordinary value of e/m.

It is possible that Brown and Barnett have used, instead of the momentum $p_x = mv_x$, what Shockley[7] calls the crystal momentum, $p_x' = \hbar k_x$, which is introduced so that the equation of motion for electron wave packets $(dp_x'/dt) = F_x$ (where F_x is the force due to the applied field) will resemble Newton's law. For this purpose $p_x' = -\hbar l_x$ is an equally convenient definition of the crystal momentum. The total crystal momentum is

$$P_x' = -\hbar \Sigma_o l_x = \hbar \Sigma_u l_x. \tag{7}$$

It is more convenient to carry out the summation over the unoccupied states for which Eq. (2) is applicable. According to Eqs. (2) and (4), $v_x = (\hbar/m^*)l_x$, so that

$$P_x' = m^* \Sigma_u v_x.$$

Replacing $\Sigma_u v_x$ by means of Eq. (3), one obtains

$$P_x' = -(m_{\text{eff}}/e)j_x, \tag{8}$$

where $m_{\text{eff}} = -m^*$ is the effective mass of electrons for which the energy levels are given by Eq. (2). Equation (8) for P_x' resembles Eq. (6) for P_x except that the electron mass is replaced by the effective mass, and since m_{eff} is negative P_x' is in the same direction as j_x.[8] The use of the crystal momentum P_x' instead of the actual momentum P_x in the conservation conditions for the coil employed by Brown and Barnett would seem to account for the remarks in their paper that the writer considers misleading.

Electron-inertia experiments do not reveal the energy levels in metals. This is consistent with the modern theory of solids and in particular with the accepted explanation for positive Hall coefficients.

[1] Sheldon Brown and S. J. Barnett, Phys. Rev. **87**, 601 (1952).
[2] R. Peierls, Z. Physik **53**, 255 (1929).
[3] See, for example, *International Critical Tables* **6**, 416 (1929); I. K. Kikoin, Physik. Z. Sowjetunion **9**, 1 (1936): Pugh, Rostoker, and Schindler, Phys. Rev. **80**, 688 (1950); J. P. Jan and H. M. Gijsman, Physica **5**, 277 (1952).
[4] C. G. Darwin, Proc. Roy. Soc. (London) **A154**, 61 (1936).
[5] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936).
[6] The symbol "e" as employed in this note represents the magnitude of the electronic charge.
[7] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, New York, 1950).
[8] See, for example, N. Rostoker, Am. J. Phys. **20**, 100 (1952), where this point is discussed in detail. (The term "momentum" in that paper should be replaced by "crystal momentum" in order to be consistent with present terminology.)

Interpretation of e/m Values for Electrons in Crystals

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A RECENT investigation[1] by Brown and Barnett of e/m for electrons in molybdenum and zinc by an inertial method has shown that the charge to mass ratio is that of an electron. It is the purpose of this letter to point out that this is the result expected from the theory of electronic conductivity; the new and precise experimental results are in excellent agreement with the theory and do not require any modification of the interpretation of the anomalous or positive Hall effect.

The paradox that e/m is negative in the Brown-Barnett experiment and positive in the Hall effect experiment is due to the fact that two different meanings m_B and m_H should be associated with the symbol m.

The fact that m_B should be taken as the electron mass follows at once from the theory of both holes and electrons in semiconductors and for electronic conduction in general.[2] In fact, the current due to "positive carriers" or "holes" is simply a shorthand way of dealing with the combined actions of many electrons. Hence, the ratio of current density to momentum density is simply $-e/m$, where $e = |e|$ is the electronic charge and m the electronic mass.[3]

On the other hand, if one could view the behavior of an isolated hole in a semiconductor under the influence of electric and magnetic fields, one would conclude that its behavior was that of a particle of charge $+e$ and a positive mass.[4] The behavior of small groups of holes introduced by light or injection in germanium has, furthermore, put these theoretical conclusions on a sound operational footing.[5]

Certain other consequences of the theoretical model show, however, that the hole should not be considered to have positive mass. For example, one readily concludes that if the mass of a natural and perfect germanium crystal is M, then adding one electron gives it a mass $M+m$ and adding one hole $M-m$. The weights and

momenta of the crystal will be consistent with these masses. Evidently, a gravitational field exerted on a stationary crystal will cause electrons to be drawn downwards and holes upwards.

An electron (respectively, hole) wave packet moving in a stationary crystal with group velocity v_g imparts a momentum mv_g (respectively, $-mv_g$) to the system. Thus, upon collision with phonons, a hole transfers momentum to the rest of the system as if it had a negative mass.

The consequences discussed above arise simply from the fact that conduction by both "excess electrons" and "holes" is really produced by electrons. The magnitude of the effective mass to use in conductivity theory depends on more complicated aspects of the interaction of the electron waves and the crystal. It is highly probable, for example, that the "effective masses" for electrons and holes in germanium cannot be described by one number each but must be regarded from a much more sophisticated viewpoint.[6]

[1] Sheldon Brown and S. J. Barnett, Phys. Rev. **87**, 601 (1952).
[2] This general conclusion has been expressed by C. G. Darwin, Proc. Roy. Soc. (London) **A154**, 61 (1936).
[3] For the case of one hole, this follows directly from Eqs. (2) and (3) on page 179 of W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950).
[4] Negative charge and negative mass do not lead to sensible results as is shown in reference 3, p. 181.
[5] See reference 3 for references to the literature and also W. Shockley, Phys. Today **3**, 16 (1950).
[6] See, for example, reference 3, p. 341.

Optical Properties of Crystalline Thoria

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THE optical properties of fused transparent crystalline thoria have been investigated. Spectroscopic analysis of the crystals showed that their purity is comparable to that of mantle grade thorium nitrate and standard thorium metal. The purity is estimated to be in the vicinity of 99.9 percent. Rather complex changes of the absorption spectrum could be observed when the specimen was heated in vacuum, oxygen, or hydrogen. Figure 1 shows the absorption spectrum (uncorrected for reflection) of a thoria crystal, which has been taken through the following cycle: (a) heating to 1800°C in vacuum, (b) heating to 1000°C in air, (c) heating to 1000°C in vacuum, (d) reheating in vacuum at 1800°C.

Heating in oxygen or air reddens the crystal and following heating in vacuum or hydrogen at 1000°C results in bleaching. The ultraviolet cutoff for these states is at 3700A. This fundamental absorption may be associated with the gap between the filled band and conduction band. The change of the absorption
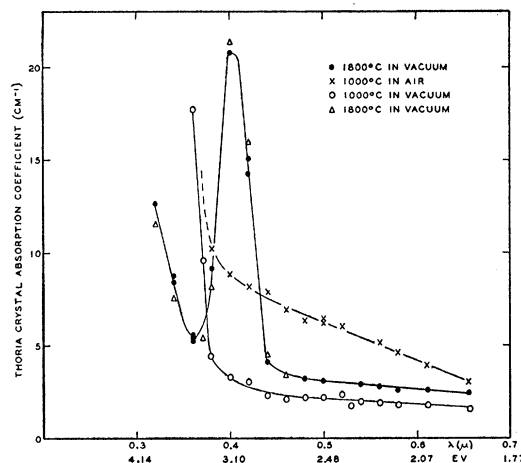

FIG. 1. Optical absorption of crystalline thoria.