Letters to the Editor

Microwave Spin Resonance Absorption by Conduction Electrons in Metallic Sodium

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We have observed conduction electron spin resonance absorption in fine particles of metallic sodium, suspended in paraffin wax, at a frequency of 9240 Mc/sec at room temperature and at 77°K. This is the first occasion, as far as we know, that conduction electron resonance has been reported.[1] The spectroscopic splitting factor g is provisionally bracketed between 1.998 and 2.004, with a probable error of ± 0.003 on these limits. The width of the resonance at half-maximum power is 78 oersteds. We believe, for reasons given below, that it will be possible in subsequent work to sharpen the resonance line considerably.

The particles were produced by a supersonic technique. The particle diameter ranged from under 10^{-4} cm to about 10^{-3} cm. A sample containing of the order of 10^{20} sodium atoms was placed in a 3-cm wavelength microwave cavity. Only a small fraction of these sodium atoms were in the microwave magnetic field, since the skin depth in sodium at the frequency used is about 10^{-4} cm. We cannot estimate closely the actual number of atoms within the skin depth in our sample since we do not know the distribution of particle size. It seems likely, however, that not more than 1 percent of the atoms were in the microwave field.

The resonance absorption is shown in Fig. 1, which is from a photograph of the CRO pattern. The horizontal scale is linear with the external magnetic field and shows the region in the neighborhood of the absorption peak. The microwave absorption puts a modulation on the vertical signal in such a way that the amplitude of the vertical signal is proportional to the resonance absorption; thus, the top of the pattern is a trace of the absorption curve of the sample. The upper signal on the trace has to do with the proton resonance equipment used to measure the external magnetic field. The small dot, approximately above the absorption maximum, is the proton resonance signal.

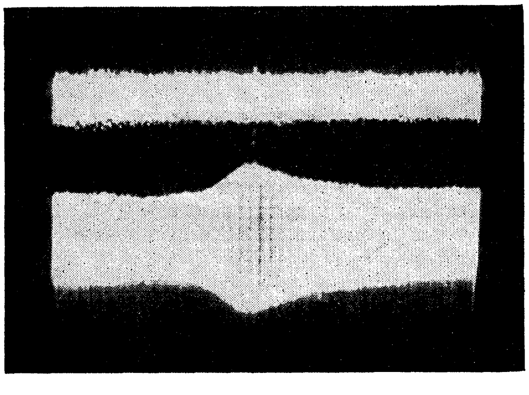

FIG. 1. Resonance absorption curve of conduction electrons in metallic sodium. Vertical scale gives absorption, horizontal scale gives applied magnetic field. At a frequency of 9240 Mc/sec, peak absorption occurs at 3304 oersteds.

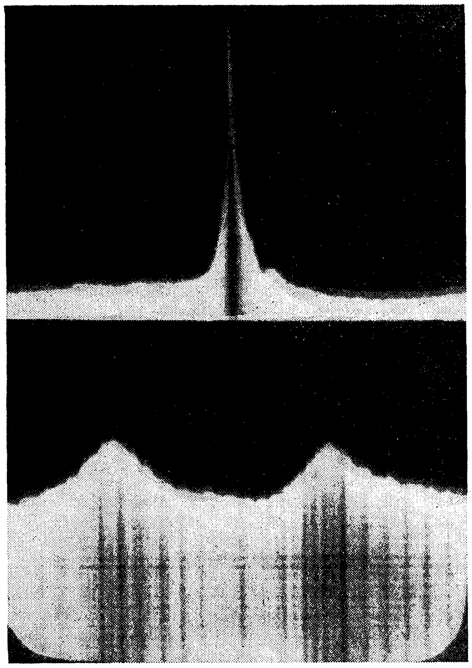

FIG. 2. Copper sulfate resonance compared to metallic sodium resonance at two temperatures. Lower curve: at room temperature; signal on left is from copper sulfate; signal on right is from metallic sodium. Upper curve: 77°K, same samples; large signal is from copper sulfate. Small signal to the right of this is from sodium. Horizontal scale is different in the two pictures.

At room temperature at 9240 Mc/sec the absorption maximum occurs at 3304 ± 5 oersteds. A small correction to the value of the field for maximum absorption must be applied because of the variation of eddy current losses with applied field.[2] Because the distribution of particle size is unknown, it is not possible to correct properly for this shift. We can, however, establish limits between which the g factor must lie by calculating the corrections for spheres with diameters small and large compared to the skin depth. Taking the particles as small, $g = 1.998 \pm 0.003$; taking the particles as large, $g = 2.004 \pm 0.003$. The theoretical free electron g is 2.0023, while Yafet[3] has calculated for the conduction electrons of sodium $g \approx 2.0019$, considering spin-orbit effects.

The close proximity of the observed g to the free electron g suggests that we are observing either the conduction electron resonance or resonance in an organic free radical or certain transition element ions. The problem of making certain that the observed resonance is in fact caused by conduction electrons and not by a paramagnetic impurity is made simple by the fact that the susceptibility of conduction electrons is temperature independent in contrast to the approximate $1/T$ dependence of ordinary paramagnetism. A comparison of relative intensities of our sodium sample compared to a small crystal of $CuSO_4 \cdot 5H_2O$ was made at room temperature and at 77°K. An amount of $CuSO_4 \cdot 5H_2O$ was put in the cavity next to the sodium sample such that the amplitudes of the two absorption peaks were approximately the same at room temperature. (Since the g factor for $CuSO_4 \cdot 5H_2O$ is different from 2.0 the two peaks are separated from each other, so that comparison is easily made.) Figure 2 shows the results of this test of absorption *vs* temperature. In the lower photograph, taken at room temperature, the left-hand peak is due to copper sulfate and the right-hand peak is due to the sodium sample. In the upper photograph, at 77°K, the large peak is from the same sample of copper sulfate, and the small peak to the right of this is the sodium resonance. The horizontal scales at the two temperatures are not the same. At 77°K the copper 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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IN 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; $-\pi/a \leq k_x \leq \pi/a$, 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 $R = 1/N_h ec$.[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

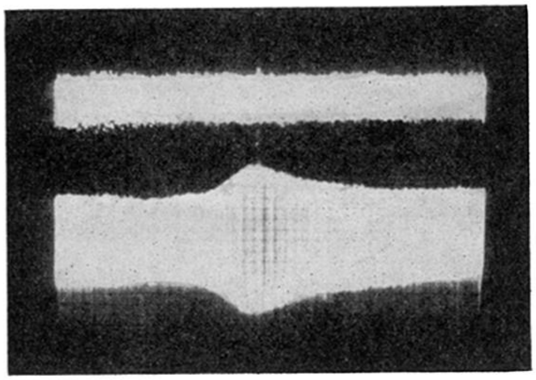
$$P_x = m\Sigma_o v_x = -(m/e)j_x, \tag{6}$$

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

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



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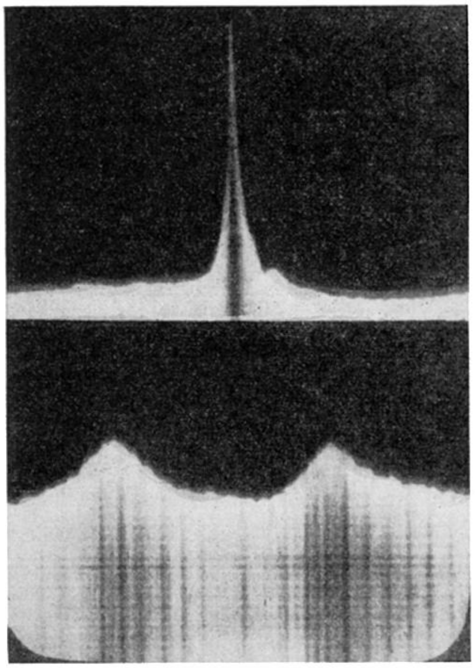

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