

state in which trace impurity atoms are present in the copper. Moreover, these results suggest that the many conflicting observations on the resistance minimum may be due to differences in the preparation of the samples.

In addition to work now in progress with dilute alloys of copper with various impurities subjected to oxidizing and reducing atmospheres, a similar study is contemplated for silver and gold. The effect of other reducing atmospheres on the

resistivity of copper is also under investigation.

\*Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

<sup>1</sup>D. K. C. MacDonald and W. B. Pearson, *Acta Met.* 3, 392 (1955).

<sup>2</sup>Blewitt, Coltman, and Redman, *Phys. Rev.* 93, 891 (1954).

<sup>3</sup>Redman, Coltman, Blewitt, and Klabunde, *Bull. Am. Phys. Soc.* 4, 150 (1959).

### MAGNETIC SPIN PUMPING IN FLUIDS CONTAINED IN POROUS MEDIA\*

H. C. Torrey

Physics Department, Rutgers University, New Brunswick, New Jersey

Jan Korringa

Physics Department, Ohio State University, Columbus, Ohio

D. O. SeEVERS

California Research Corporation, La Habra, California

and

Jean UEBERSFELD

Université de Besançon, Besançon, France

(Received September 8, 1959)

In several cases a large nuclear polarization has been produced in a fluid by pumping with microwave radiation in resonance with paramagnetic centers near a solid-fluid interface.<sup>1,2</sup> The number of such paramagnetic sites per unit volume of the sample is often very small. Only nuclei in the fluid molecules nearest to the paramagnetic centers are directly experiencing the spin flips which give rise to such an Overhauser-type effect. Therefore, molecular diffusion must play an essential role in these phenomena. In this note we derive a theoretical expression for the total nuclear polarization, which contains the fluid volume as an independent variable.

Let an amount of fluid with volume  $V$  and of spherical shape be bounded by the solid. The surface contains a number of paramagnetic centers which are in resonance with the microwave power; we denote by  $V_p$  the volume occupied by fluid molecules in the surface layer in the immediate vicinity of these centers, and by  $V_s$  (which is part of  $V$ ) the volume occupied by fluid molecules in the remainder of the surface layer. We will assume that  $V_p \ll V$ . The nuclei in  $V_p$  are flipped at a given rate by the external microwave power through the two known processes of

the Overhauser type or through that of the type reported by Uebersfeld *et al.*<sup>1</sup> and by Abragam and Proctor.<sup>3</sup> Some flipped nuclei escape to the volume  $V$  before they are relaxed. In  $V$  they are exposed to the ordinary relaxation, characterized by the relaxation time  $T_1^0$ . They also may penetrate the part  $V_s$  of  $V$ , as we assume that the fluid forms a single continuous phase. In  $V_s$  relaxation is influenced by the strongly reduced mobility of the molecules which, unless one approaches a solid-like condition, is an enhancement. Also surface magnetism not in resonance with the microwave power can contribute to the relaxation in  $V_s$ . We denote by  $T_1^s$  the relaxation time in  $V_s$ . Finally the nuclei may move back into  $V_p$  and be relaxed there, with a characteristic time  $T_1^p$ .

In a steady situation a complicated pattern of nuclear polarization will be established, given by the density  $m_0 + m(x, y, z)$ , where  $m_0$  is the equilibrium value. We wish to calculate the total excess magnetization,  $M = \int_V m dx dy dz$ . This can be obtained from two simultaneous equations, for the steady state spin polarization in  $V$  and in  $V_p$ , respectively. The coupling describes the transfer of spin polarization across their boundary. In  $V$

we use the equation<sup>4</sup> for nuclear relaxation with diffusion:

$$0 = \partial m / \partial t = D \nabla^2 m - m / T_1', \quad (1)$$

where  $D$  is the molecular diffusion constant, and  $T_1'$  is the relaxation time in  $V$  excluding the contribution from  $V_p$ . One of us<sup>5</sup> has shown that under a wide variety of circumstances in sufficiently small pores:

$$1/T_1' = 1/T_1^0 + (V_s/V)/(T_1^s + \tau_s), \quad (2)$$

where  $\tau_s$  is the sticking time of molecules entering  $V_s$ . As a boundary condition for (1) we use the condition that the flux of polarization across the surface of the sphere equals the net flux across the boundary of  $V_p$  and  $V$ :

$$4\pi R^2 D (dm/dr)_{r=R} = (V_p/\tau_p) [m_p - m(R)], \quad (3)$$

where  $R$  is the radius of the sphere,  $m_p$  is the steady state polarization density in  $V_p$ , and  $\tau_p$  is the sticking time of molecules in  $V_p$ . Finally  $m_p$  is determined by the production rate of nuclear polarization in  $V_p$ , and by local relaxation and net transfer to  $V$ :

$$0 = dm_p/dt = \rho K S^* / T_1^p - m_p / T_1^p - [m_p - m(R)] / \tau_p. \quad (4)$$

Here  $\rho$  is the nuclear density in  $V_p$ ,  $S^*$  is a measure for the electron spin polarization produced by the microwave source:  $S^* = S_z - S_0$ , i.e., the deviation of spin polarization from thermal equilibrium, for the Overhauser effect and  $S^* = S_z$  for the effect reported in references 1 and 3.  $K=1$  for the effect mentioned last under the conditions of their experiments and for the Overhauser effect due to contact interaction;  $K=-1/2$  for the Overhauser effect due to dipole-dipole interaction.

The solution of (1) which is well behaved at  $r=0$  is of the form:

$$m(r) = C \sinh u / u, \quad u = r(DT_1')^{-1/2}.$$

Using (3) and (4), we obtain in the limit that  $R(DT_1')^{-1/2} \ll 1$ :

$$M = V_p \rho K S^* T_1^0 / (T_1^p + \tau_p), \quad (5)$$

where

$$1/T_1 = 1/T_1' + (V_p/V)/(T_1^p + \tau_p).$$

This limiting condition which makes the result independent of the shape, is also a requirement for the validity of (2). Equation (5) also holds obviously when  $V$  is very large and at the same time  $T_1 \approx T_1^0$ .  $T_1$  as given by (6) is, by analogy with (2), seen to be the experimentally observable relaxation time of the fluid in the pore.

One can distinguish two cases:

Case 1.  $T_1 \ll T_1^0$ :

$$M = V \rho K S^* \left[ 1 + \frac{V_s}{V_p} \left( \frac{T_1^p + \tau_p}{T_1^s + \tau_s} \right) \right]^{-1}, \quad (7)$$

Case 2.  $T_1 \approx T_1^0$ :

$$M = V_p \rho K S^* T_1^0 / (T_1^p + \tau_p). \quad (8)$$

Case 1, which applies when the surface relaxation dominates, describes an enhancement of the nuclear resonance absorption by a factor independent of  $V$ . One obtains the full Overhauser effect if relaxation in  $V_p$  dominates,  $V_s/(T_1^s + \tau_s) \ll V_p/(T_1^p + \tau_p)$ . If relaxation in  $V_s$  dominates, one finds a reduced effect. This may be realized, e.g., if the electron resonance is inhomogeneously broadened. In case 2, i.e., when the bulk relaxation dominates,  $M$  is independent of  $V$  so that the observed enhancement factor varies as  $V^{-1}$ . This may apply when  $V$  is made very large compared with  $V_p$  and  $V_s$ , or when  $\tau_p$  and  $\tau_s$  are very long. One may conclude that the study of spin pumping in these systems gives rather detailed information concerning relaxation at the surface.

\*Work was performed in the La Habra Laboratory of the California Research Corporation.

<sup>1</sup>Erb, Motchane, and Uebersfeld, Compt. rend. 246, 2121 (1958).

<sup>2</sup>J. P. Borel and P. Cornaz, Compt. rend. 247, 1988 (1958).

<sup>3</sup>A. Abragam and W. G. Proctor, Compt. rend. 246, 2253 (1958).

<sup>4</sup>H. C. Torrey, Phys. Rev. 104, 563 (1956).

<sup>5</sup>H. C. Torrey (to be published).