

occurs, even though they are randomly distributed. A given solute spin will be polarized up or down depending on its location relative to the phase of the spin density wave, which necessarily has long-range coherence. Since the wavelength of the wave is incommensurate with the lattice parameter, the solute spins will experience a distribution in molecular fields  $B$  varying from  $-Gb$  to  $Gb$  according to the probability distribution

$$P(B) = (G^2 b^2 - B^2)^{-1/2} / \pi. \quad (11)$$

The thermodynamic properties of such a system may be derived in a straightforward manner. One finds

$$kT_c = 3\xi S(S+1)G^2 c / 32C, \quad (12)$$

where  $c$  is the solute concentration. This result is in excellent agreement with experiment. The low-temperature magnetic specific heat  $C_M$  is proportional to temperature:

$$C_M = \gamma_M T, \quad (13)$$

where

$$\gamma_M = 32\pi^2 N C k^2 / 27G^2 (2S+1)\xi. \quad (14)$$

The outstanding feature is that  $\gamma_M$  is independent of solute concentration. Recent experiments of J. E. Zimmerman (to be published) give remarkable confirmation of this result for Cu-Mn alloys having solute concentrations from 1/6 to 4 atomic percent. This linear specific heat is a direct consequence of the distribution (11). The reason is that each incremental increase in  $T$ , from  $0^\circ\text{K}$ , allows a new group of solute spins to reach the temperature at which they become thermally disoriented, and the integrated heat capacity of such a group is proportional to the temperature at which disorientation occurs. The lack of concentration dependence results from the fact that the spin density wave amplitude is proportional to  $c$ , so that  $cNP(0)$  is independent of  $c$ . The magnetic specific heat is approximately linear in  $T$  all the way to  $T_c$ , at which point it drops to 0.  $T_c$  is about  $25^\circ\text{K}$  per atomic percent.

The anomalous electric, magnetic, and resonance properties of Cu-Mn alloys can be understood within the framework of this theory. They will be elaborated in detail in future publications.

## RESISTANCE MINIMUM AND RESISTIVITY OF COPPER AT LOW TEMPERATURES

S. T. Sekula

Solid State Division, Oak Ridge National Laboratory,\* Oak Ridge, Tennessee

(Received August 3, 1959)

The existence of an electrical resistance minimum in copper has been ascribed to the presence of small concentrations of specific metallic solutes in the metal by some workers,<sup>1</sup> while others have suggested structural defects in the metal as playing a major role.<sup>2</sup> Recently Redman *et al.* had demonstrated that the resistivity of single crystals of copper is markedly dependent on their thermal history.<sup>3</sup> In particular, the resistivity at the normal boiling point of He was found to decrease with increasing exposure time in an annealing treatment at  $700^\circ\text{C}$  in  $30 \mu$  of air and would attain a constant value after five hours of heat treatment. A re-examination of the earlier work on the resistance minimum in copper<sup>2</sup> in light of these new data suggested the possibility that the resistance minimum was influenced by the hardness of the vacuum during the annealing treatment. MacDonald and Pearson<sup>1</sup> also ob-

served that the anomalous resistivity minimum seemed strongly dependent on reducing or oxidizing atmospheres during the melting of copper. A study of the role of the annealing atmosphere on the electrical resistivity minimum of copper was therefore felt to be of considerable interest.

The experimental techniques for these measurements are sketched briefly here with a detailed description reserved for later publication. The samples consisted of 0.05-cm diameter copper wire of 25-cm length wound around a quartz tube. The specimens were annealed in an evacuated mullite tube which allowed for annealing in desired atmospheres by means of a controlled leak. The resistance measurements were made on a Wenner potentiometer. Provisions for pumping on the He bath and a heater coil around the thermometer bulb which also served as the sample container enabled a temperature range to be

covered from 1.7°K to 25.0°K.

One particular sample of copper was subjected to eleven heat treatments in alternate oxidizing and reducing atmospheres. In every case annealing in a reducing atmosphere increased the overall resistivity and brought on a resistance minimum. Annealing in an oxidizing atmosphere reduced the resistivity and washed out the minimum. Curve 1 of Fig. 1, which is typical after a reducing treatment, was obtained by annealing the sample in a graphite boat in a vacuum of  $2 \times 10^{-5}$  mm Hg. A resistance minimum is found at about 12.5°K and an abrupt increase in the resistivity is seen in the region from 6°K to 8°K. The sharp rise was found to be due to the method of attaching electrical contacts to the sample and is incidental to the appearance of the resistance minimum. A typical curve following an air anneal (10 microns at 750°C for 2 hours) is shown in Curve 2 of Fig. 1. The resistivity at 4.2°K has decreased by approximately a factor of five and the minimum is not observable. An activation analysis revealed the presence of iron as the major impurity and smaller amounts of silver

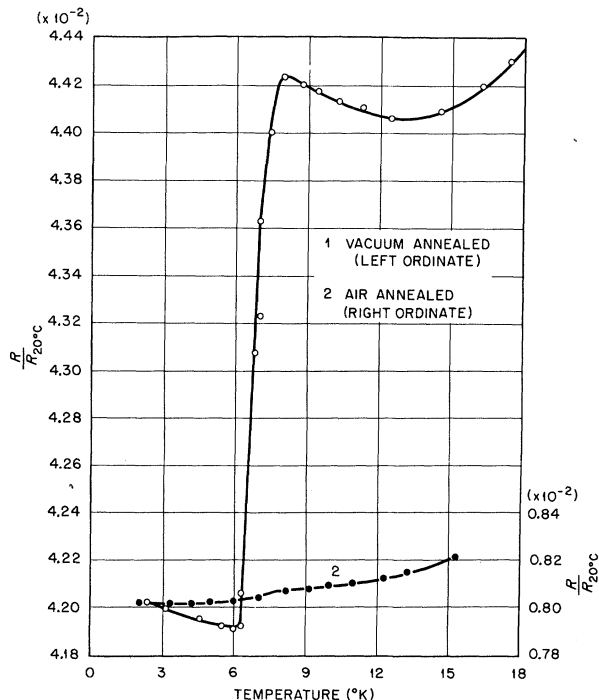


FIG. 1. The temperature dependence of the resistivity of copper with a small impurity content after annealing in a reducing atmosphere and an oxidizing atmosphere. (The sharp rise in resistivity was found to be due to the method of attaching electrical leads. Spot-welded leads removed this rise but did not affect the curves elsewhere.)

and zinc. Unfortunately it was not possible to obtain numerical values for these concentrations.

Similar results were found in a copper sample of much higher purity. In this case the specimen was annealed in a vacuum of  $2 \times 10^{-5}$  mm Hg at 950°C for two hours and was found to have a resistance minimum as shown in Fig. 2. It should be noted that the low resistivity of this sample following the treatment in a reducing atmosphere is an indication of high purity. The results upon reheating this specimen in 10  $\mu$  of air at 750°C for two hours are also shown in Fig. 2. The resistivity minimum is no longer observed and the residual resistivity is seen to have decreased approximately by a factor of three.

These results, while not completely understood, indicate the strong influence of trace impurities on the residual resistance and the resistance minimum of copper at low temperatures. It is particularly significant in this regard that the anomalous resistivity minimum is reversible and can be introduced or removed at will by a heat treatment in an appropriate atmosphere. These results would then seem to show clearly that the resistance minimum is not a fundamental property of the copper but a manifestation of the

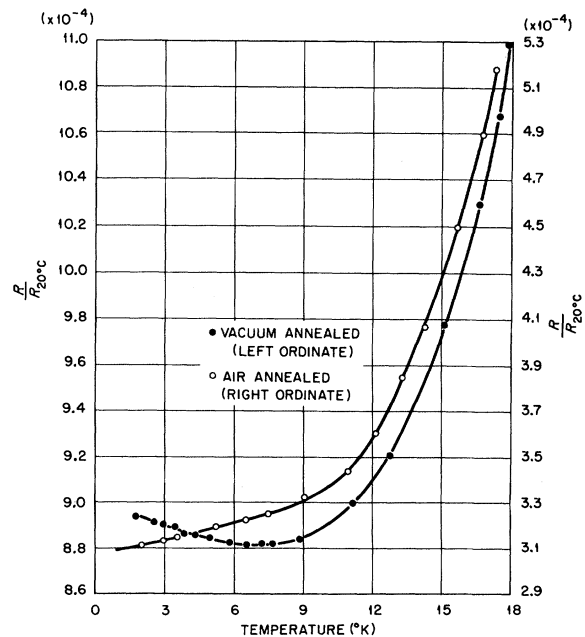


FIG. 2. The temperature dependence of the resistivity of 99.999% pure copper (American Smelting and Refining) after annealing in a reducing atmosphere and an oxidizing atmosphere.

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  $V$