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# The effect of pressure on the electrical resistance of copper at low temperatures

Prug. Roy. Soc (London), A, 241, 397 (1957)

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(Communicated by N. F. Mott, F.R.S.-Received 5 March 1957)

The resistivity of copper under hydrostatic pressures up to 3000 atm has been measured at temperatures between  $4^{\circ}$  K and room temperature. Two specimens of commercially pure copper (99.98%) and an alloy of 0.056 at. % iron in copper were studied, the alloy being chosen because it showed a large resistance minimum.

The effect of pressure on the ideal resistivity is in good agreement with Grüneisen's theory. There were some theoretical reasons for expecting that the alloy would have a large pressure coefficient of resistivity at or below the temperature of the resistance minimum. The pressure coefficient at these temperatures was, however, quite small and similar in value to the pressure coefficients of residual resistivity of the two purer specimens.

Both the residual resistivity of the alloy and its pressure coefficient appeared to be strongly dependent on temperature.

#### 1. INTRODUCTION

The electrical resistance of copper at low temperatures is of particular interest; quite small traces of certain impurities in copper cause the resistance of the specimen to increase with falling temperature instead of becoming constant as theory predicts. The actual temperature at which the minimum of resistance occurs depends on the kind of impurity and its concentration (MacDonald 1952; MacDonald & Pearson 1955); it usually lies between about 10 and 25° K. The rise in resistance below the minimum likewise depends on the kind and concentration of impurity, and in some cases the rise is comparatively large.

MacDonald & Pearson (1953, 1954) have shown that an unusually large thermoelectric power at low temperatures is associated with this strange resistive behaviour and have suggested that this effect would in turn be associated with an abnormally large pressure coefficient of resistance at low temperatures. Consequently, we have measured at very low temperatures the pressure coefficient of a dilute copper alloy showing a typical resistance minimum. Both for the sake of comparison and for its own intrinsic interest we have also measured the pressure coefficient at these temperatures of two quite pure samples of copper which did not exhibit the resistance minimum. The following is an account of these experiments and their results.

#### 2. EXPERIMENTAL METHOD

One difficulty inherent in all attempts to measure pressure effects at low temperatures is to find a suitable pressure-transmitting medium. Ideally, of course, we should like to have a true fluid of low viscosity, but this is not possible because all substances become solid under pressure at low enough temperatures. We have therefore chosen to use helium as the pressure medium because at a given pressure it retains its ideal fluid characteristics down to a lower temperature than any other

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[ 397 ]

26-2

substance, and also because even in the solid phase it can be used to transmit pressure. The technique and the apparatus have been described in detail elsewhere (Dugdale & Hulbert 1957), but two important features should be emphasized here First, the pressure is always applied, and any change of pressure is always made with the helium in the fluid state. Second, the helium is solidified and subsequently cooled at constant volume. In this way the pressure in the solid can be deduced from its equation of state (Dugdale & Simon 1953) and, in addition, any temporary nonhydrostatic stress on the specimen is minimized.

The maximum pressure at present available to us in the fluid phase is about3000 atm and in the solid phase about 2000 atm. Consequently, since copper is relatively incompressible, the effects to be measured are small, of the order of 0.3 a resistance change under the highest pressure. Moreover, at most temperatures the temperature dependence of the resistance is considerable, e.g. the copper + iron alloy at  $4\cdot2^{\circ}$  K has a negative temperature coefficient of almost 1 %/deg.\* It is therefore clear that the temperature of the specimen must be kept very constant or if it changes, it must be accurately measured. We have in fact used both methods. Where a suitable temperature bath was available (at the helium and the nitrogen boiling points) the high-pressure bomb was immersed directly in the liquid and true isothermal experiments were made; at other temperatures, however, the bomb wasurrounded by a vacuum and the precise temperature was not controlled but measured. The former method was not very convenient at the helium point becausof the need to raise the bomb temperature to the helium melting point in order to change the pressure.

The smallness of the effects to be measured determined both the method of measurement and the size of specimens. To measure the resistance we used a potentiometer accurate to  $\frac{1}{10} \mu$ V. In general, the measuring currents were limited by the heating effects which could be tolerated without upsetting the thermal equilibrium between the specimen and the platinum or carbon resistance thermometer attached to the outside of the bomb. Currents of up to several hundred milliamperes were used. The minimum value of the resistance to be measured was about 0.01  $\Omega$ , and so in this way we were able to secure an accuracy of resistance measurement of about 5 parts in 10<sup>5</sup> at the lowest temperatures. The pressures were measured by a Bourdon gauge subsequently calibrated against a pressure balance. In general, the accuracy of the measurements was limited by the accuracy of the resistance measurementby the temperature control, or in some cases by the reproducibility of the specimetthemselves.

#### 3. THE SPECIMENS

None of the specimens was heat-treated by us before measurement; all of them were polycrystalline. They were loosely mounted on an insulated copper former.

## Sample I

This was a specimen of commercial copper with a residual resistance ratio.  $R_0/R_{273}$ , of  $9.3 \times 10^{-3}$  (cf. Dauphinee & Preston-Thomas 1954). The impurities a

\* This large temperature coefficient suggests that the alloy might make a useful resistant thermometer in the temperature range between 4 and 20° K.

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This was a cop Dr W. B. Pearson ments below 1° K resistance at the n It was chosen be a truly hydrostatic ture before the he The dimensions (average); thickne

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\* Specimens I at  $\sim 530^{\circ}$  C for 16 h. sample II,  $4.3 \times 10^{\circ}$  only to changes in annealing process than the physical

398

determined by spectral analysis were: iron ~ 0.01 %; traces of zinc and possibly magnesium and silicon. The specimen consisted of about 8 m of 36 B. and S. gauge wire insulated with Formel varnish. The grain size appeared to be about  $10^{-2}$  mm. X-ray examination (for which we are indebted to Dr E. G. Eeles) showed that the grains had a marked preferred orientation.

#### Sample II

This was a specimen of commercial copper slightly purer than sample I, having a residual resistance ratio of  $7 \cdot 0 \times 10^{-3}$ . The impurities determined by spectral analysis were: iron < 0.01 %; traces of zinc and possibly magnesium and silicon. This specimen was made from about 5 m of 34 B. and S. gauge wire, double-cotton covered. The grain size of this specimen was about  $10^{-2}$  mm; X-ray examination showed a slightly less marked preferred orientation in this case.\*

#### Sample III

This was a copper-iron alloy containing 0.056 at. % iron. It was prepared by Dr W. B. Pearson of these laboratories and had been used previously for measurements below 1° K. (For details of the preparation, see Pearson 1955.) The ratio of its resistance at the minimum  $(26.6^{\circ} \text{ K})$  to that at the ice point was  $2.3 \times 10^{-1}$ .

It was chosen because the temperature of the minimum was sufficiently high that a *truly hydrostatic* pressure up to about 2500 atm could be applied at this temperature before the helium would solidify.

The dimensions of the specimen were as follows: length 27.4 cm; breadth 0.115 cm (average); thickness 0.0095 cm (average).

## 4. THE EXPERIMENTAL RESULTS

Table 1 shows a summary of the measurements made on the three copper samples; all the changes of resistance were linearly dependent on pressure within the experimental accuracy. Because reference is made in the discussion to both the temperature and pressure coefficients of resistance, both these quantities have been tabulated for those temperatures at which they were measured.

The pressure coefficient of residual resistance of sample I was measured in two ways. In the first, the pressure was applied by means of solid helium and the resistance at  $4\cdot5^{\circ}$  K was determined. In the second, the measurements were made in the neighbourhood of 10° K making use of the fluid properties of helium which at this temperature are retained up to 500 atm pressure. At 10° K the thermal component of resistance in this specimen was still only a very small fraction of the total. Figure 1 shows a comparison between these two sets of measurements and figure 2 shows some of the measurements of the resistance of sample III in the neighbourhood of the minimum.

\* Specimens I and II were subsequently annealed by heating in a helium atmosphere at  $\sim 530^{\circ}$  C for 16 h. Their residual resistance ratios were then as follows: sample I,  $2.8 \times 10^{-3}$ ; sample II,  $4.3 \times 10^{-3}$ . Unfortunately, it is not possible to be sure that these changes are due only to changes in physical defects. The large change in sample I might indicate that the annealing process had changed the chemical purity (see MacDonald & Pearson 1955) rather than the physical state of the metal.

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		$1  \mathrm{d}R$	$1  \mathrm{d}\rho_i$	$dR^{\dagger}$	$T \mathrm{d}  ho_i$	()n the first, t
	R	$\overline{R}  \mathrm{d} p_{\mathrm{obs.}}$	$\overline{\rho_i}  \mathrm{d}p$	dTobs.	$\rho_i dT$	
T (°K)	(Ω)	(%/1000 atm)	(%/1000 atm)	(Ω° C <sup>-1</sup> )		
		S	ample I			
298.6	11.0826	-0.214	$-0.240 \pm 0.005$	$43.1 \times 10^{-3}$	1.17	1 1 2 2 2
83.5	1.6086	-0.35	$-0.396 \pm 0.01$	42.6	2.35	
61.5	0.75778	-0.46	$-0.554 \pm 0.02$	32.1	2.97	0
25.1	0.11462	-0.09	$-0.80 \pm 0.04$	3.73	4.42	G
9.75	0.093727	+0.065	-	0.123	4.3	CO
4.2	0.093447	+0.067	$+0.045\pm0.01$	0.0	-	tan
		SE	ample II			osis
293.5	2.7249	-0.170	$-0.195 \pm 0.005$	$10.9 \times 10^{-3}$	1.18	Ĥ
78-2	0.34336	-0.333	$-0.374 \pm 0.005$	$10.2 \times 10^{-3}$	2.45	
4.2	0.017490	+0.05	$+0.031\pm0.01$			
4.2§	0.017550	+0.03	$+0.01 \pm 0.01$			
		sa	mple III			· · · · · · ·
291-1	0.060500	$-0.189 \pm 0.004$		$19.4 \times 10^{-5}$		
80-0	0.019641	$-0.080 \pm 0.01$		17.7		
78.0§	0.019468	$-0.068 \pm 0.004$				FIGURE 2. The
26.5	0.013256	$+0.041 \pm 0.005$		0.0		the minim
4.5	0.014808	$+0.03 \pm 0.03$		-12.5		22 Novemb
4.28	0.015048	+0.056 + 0.015		_		

# TABLE 1. THE TEMPERATURE AND PRESSURE COEFFICIENTS

<sup>†</sup> The error in these values is about 1 % except at the lowest temperature where it rises to about 2%.

‡ Pressure coefficient of residual resistivity.
§ In liquid baths.

400



FIGURE 1. The pressure dependence of the resistance of copper (sample I). (a) shows measure ments of the residual resistance using solid helium as the pressure-transmitting medium. and (b) shows measurements of residual resistance at 9.75° K under truly hydrostatic pressure (see text). The open points represent measurements made with increasing pressure and the solid points those with decreasing pressure.

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E COEFFICIENTS R  $dR^{\dagger}$  $T d\rho_i$ dTobs.  $\rho_i dT$  $(\Omega^{\circ} C^{-1})$  $43.1 \times 10^{-3}$ 1.17 42.6 2.35  $32 \cdot 1$ 2.97 3.73 4.42 0.1234.3 0.0  $10.9 \times 10^{-3}$ 1.18  $10.2 \times 10^{-3}$ 2.45 $19.4 \times 10^{-5}$ 17.7 0.0 -12.5temperature where it rises to



imple I). (a) shows measureessure-transmitting medium, 'K under truly hydrostatic ients made with increasing The behaviour of sample II at low temperatures requires special mention. The effect of pressure on its residual resistance was measured on two separate occasions. On the first, the results, while not strikingly unusual, showed a greater scatter than



FIGURE 2. The resistance of a copper-iron alloy (0.056% iron) in the neighbourhood of the minimum at various pressures. 

neasured 20 November 1956; ○, measured 22 November 1956.



FIGURE 3. The pressure coefficient of the ideal resistivity of copper as a function of temperature. ●, sample I; ○, sample II; ▲, Bridgman's values. The continuous line shows the values based on Grüneisen's theory.

we had expected. These first measurements were made with the bomb in a vacuum jacket. We decided then to repeat the experiment with the bomb immersed directly in the liquid helium. We found that on the first application of pressure (about 2000 atm at  $4 \cdot 2^{\circ}$  K) the resistance rose in the normal way. On releasing the pressure the resistance did not diminish to its starting value but rose still more. Because

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control of the temperature of the bomb is difficult without a vacuum jacket, we had inadvertently cooled the bomb very rapidly after changing the pressure. We thought this might have caused strain and a consequent increase in resistance both on solidification and melting of the helium; we therefore re-applied the pressure and took care to cool the bomb slowly through the solidification region of the helium. This time the resistance fell on releasing the pressure, though not quite to its original value.

This kind of behaviour recalls that found by Hatton (1955) in his experiments on residual resistance using solid hydrogen as the pressure transmitting medium. The order of magnitude of the effect in our experiments could certainly be accounted for by slight non-hydrostatic straining of the specimen (cf. Pearson 1954), and it may be that this is the cause of the 'permanent' changes of resistance in Hatton's specimens. Because small non-hydrostatic strains may have such relatively large effects it is reassuring that the results on sample I by the solid helium method agreed well with those using truly hydrostatic pressure.

Finally, it should be noted that the pressure coefficients of 'ideal' resistance derived from samples I and II are appreciably different from each other and from those of Bridgman (see figure 3). We do not at present understand the reason for this.

#### 5. DISCUSSION; COMPARISON WITH THEORY

In comparing our experimental results with the predictions of theory it is convenient to consider separately the effect of pressure (a) on the thermal component of resistance—the so-called 'ideal' resistance, (b) on the residual resistance, and (c) on the resistance minimum.

## (a) Pressure coefficient of the ideal resistance of copper

#### (i) The temperature dependence of the pressure coefficient

In considering the pressure dependence of the equilibrium properties of solids, the Grüneisen model of a solid has proved of great value. A Grüneisen solid may be defined as one in which the entropy dependence on temperature and volume has the following functional form:  $S = S(\theta/T)$ , where  $\theta$  depends only on the volume. If the entropy is of this form then it becomes possible to relate the isothermal pressure dependence of the entropy to the temperature dependence of the entropy, i.e. the thermal expansion to the specific heat. This gives, in fact, Grüneisen's law of thermal expansion. The only quantity involved other than readily measurable thermodynamic quantities is the volume or pressure dependence of  $\theta$ . (The Grüneisen relation is indeed frequently used to obtain a measure of this dependence.)

In a precisely similar manner, we find that the pressure dependence of the ideal resistivity of a metal is most easily discussed in terms of an analogous Grüneisen metal, i.e. one in which  $\rho_i = (K/T)f(\theta_R/T)$ .\* Here K is a quantity which is independent of temperature but may change with pressure, and  $\theta_R$  is a temperature which is characteristic of the resistive behaviour of the metal and assumed to depend only on volume. If this assumption is valid then it becomes possible to relate the pressure

\* There are theoretical reasons for expecting this form of temperature dependence, see MacDonald (1956).

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By making about the latt between  $d\rho_i/c$ dependence of theoretical for experiment (cl pressure coefficient temperature co

To obtain a expression der that  $d \ln \theta_R / dp$  expansion coel volume. In wh

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\* The function \* The function † In that case. the change of corelatively small.

402

dependence of  $\rho_i$  to the temperature dependence of  $\rho_i$ . Of course, this again involves the pressure dependence of  $\theta_R$ . The relation is

$$\frac{1}{\rho_i} \frac{\mathrm{d}\rho_i}{\mathrm{d}p} = \frac{1}{K} \frac{\mathrm{d}K}{\mathrm{d}p} - \frac{\mathrm{d}\ln\theta_R}{\mathrm{d}p} \left\{ 1 + \frac{\mathrm{d}\ln\rho_i}{\mathrm{d}\ln T} \right\}.$$
(1)

By making various simplifying assumptions about the electron behaviour and about the lattice it is possible to find a theoretical form for  $f(\theta_R/T)$ . Relation (1) between  $d\rho_i/dp$  and  $d\rho_i/dT$ , however, depends only on the type of functional dependence of  $\rho_i$  on T and not on its precise form. It happens that with copper the theoretical form of the temperature dependence of  $\rho_i$  is very close to that found by experiment (cf. Kelley 1954) so that it does not matter whether one compares the pressure coefficient of resistivity with the theoretical or the measured values of the temperature coefficient.

To obtain a value of  $d \ln \theta_R/dp$  we assume that it is the same as the corresponding expression derived from the Grüneisen law of thermal expansion, i.e. we assume that  $d \ln \theta_R/dp = 3\alpha V/C_v$  and is independent of temperature. Here  $3\alpha$  is the volume expansion coefficient,  $C_v$  the atomic heat at constant volume and V the atomic volume. In what follows we have taken  $d \ln \theta_R/dp = 1.4 \times 10^{-6} \text{ atm}^{-1}$ .

To compare this theory with experiment we plot  $\frac{3\alpha V}{C_v} \left\{ 1 + \frac{d \ln \rho_i}{d \ln T} \right\}$  against T using for convenience the theoretical value of  $(1 + d \ln \rho_i/d \ln T)^*$  with  $\theta_R = 320^\circ$  K.

On the same graph we show the experimental values  $(1/\rho_i) d\rho_i/dp$  derived from our own measurements and also from those of Bridgman (1917, 1932, 1937). We have made a small correction to Bridgman's results to allow for the change of residual resistance with pressure, the correction being assumed the same as for our sample II which appears to be most directly comparable with Bridgman's specimen.

If all the assumptions which we have made were strictly valid, the experimental and theoretical curves would be separated by a constant amount equal to (1/K) dK/dp. The separation above 100°K is in fact very constant for the different specimens, but too much emphasis should not be placed on this because, strictly, we should compare pressure coefficients all measured at the same volume.<sup>†</sup> Below 100°K the deviations from the theoretical curve become more marked and might well be attributed to an increase of  $(1/\theta_R)/d\theta_R/dp$  with falling temperature, since deviations from the Grüneisen law of thermal expansion are indeed found at low temperatures (see Figgins, Jones & Riley (1956) for the most recent work). It is also known that copper shows departures from the Bloch-Grüneisen law of electrical resistance at very low temperatures so that in this region the theory is not so valuable as at higher temperatures.

Despite these relatively minor discrepancies it is clear that the main features of the temperature variation of the pressure coefficient are very well accounted for by Grüneisen's theory.

\* The function is tabulated by Grüneisen (1941) in an earlier paper on some aspects of the present problem.

<sup>†</sup> In that case, presumably, the value of  $d\ln \theta_R/dp$  would also be altered. These effects and the change of compressibility with temperature have been neglected because they are all relatively small.

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#### (ii) The pressure dependence of the interaction constant, K

From figure 2 we can deduce a value for (V/K) dK/dV; it lies between -0.8 and -1.4. A review of the theoretical calculations of this coefficient has been given by Lawson (1956) and from this it appears that estimates based on the assumption of free electrons give values in the neighbourhood of -1. The assumption of free electrons is of course very reasonable in the case of copper.

A more significant agreement with theory is the approximate constancy of the coefficient above 100°K. Deviations below this temperature might perhaps be ascribed to a change in the 'binding' of the electrons but this is unlikely; it is more probable, as we have indicated above, that failure of the Grüneisen law of thermal expansion is the cause of this discrepancy.

#### (b) The pressure coefficient of residual resistivity

There has been considerable experimental work at room temperature on the pressure and temperature coefficients of the residual resistance of alloys of the noble metals (Linde 1939, 1949); this has been summarized in a recent review article by Gerritsen (1956). In these experiments the concentration of 'impurity' was usually a small atomic percentage. Linde found that, broadly speaking, alloys of the noble metals with non-transition elements had negative pressure coefficients\* all of rather similar magnitude (about -0.05% per 1000 atm, corresponding to  $d \ln \rho_0/d \ln V \sim +1$ . Linde has accounted for these results in a semi-quantitative manner using Mott's expression for the resistance due to a given small concentration of screened impurity ions (Linde 1949), and Friedel (see, for example, Friedel 1956) has correlated these pressure coefficients with the corresponding thermo-electric power measurements at room temperature.

The effects of pressure on the residual resistance produced by transition elements in copper, silver and gold are much more complicated (Linde 1949). The pressure coefficient depends both in magnitude and sign on the kind of impurity atom which produces the resistance and it is scarcely possible to make any generalization from these results. In several alloys a positive pressure coefficient of residual resistivity is associated with a negative temperature coefficient, and Linde correlated some of these by assuming that the resistance change with temperature arises from the volume change due to thermal expansion. He also suggested that a process analogous to the Ramsauer effect in gases (i.e. an *increase* in electron scattering with increasing electron velocity) might be important in explaining the complex behaviour of these alloys.

Lenssen & Michels (1935) derived a theoretical expression for the volume dependence of residual resistivity due to either chemical or physical impurities. On the assumption of free electrons and that the scattering cross-section is effectively independent of pressure they deduce that  $d \ln \rho_0/d \ln V = -\frac{1}{3}$ , and that this parameter is independent of the specific solvent or solute. These assumptions are evidently too drastic.

\* Among those studied, Zn in Au and possibly Mg in Ag had positive pressure coefficients.

#### Pressure

Experimentall  $\geq -0.3$ . It is difficult to the impurity it is all because they sho a resistance miniin solid solution difference betwe for by the difference

	10	)
$T(^{\circ} \mathbf{K})$		1
291.1	42.4	1.1
S0.0	5.47	
78.0	5.15	1.514
26.5	0.108	-
$4 \cdot 2$	-	-
$\dagger dR_0/d$	dT = 2	1
‡ We h	nave use	d

In sample II Because the im able to make so of both this resi the total resisti.  $t_L$  is not change of  $\rho_0$  at severa  $\rho_{\text{outal}} = \rho_i + \rho_0).$  $(1 p_i) dp_i / dp, w$ of  $(1/\rho_0) d\rho_0/dp$ table 2. We find from its low ter changed sign a reports no pres his results on temperature (at un sign to that c ame size, in fa

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Experimentally we find that, for sample I,  $d \ln \rho_0/d \ln V \simeq -0.7$  and for sample II,  $\simeq -0.3$ . It is difficult to know what are the predominant scattering processes that contribute to the residual resistances; although iron is nominally the dominant impurity it is almost certainly not present in solid solution in these two specimens because they show no resistance minimum (cf. Pearson 1955). Zinc does not produce a resistance minimum in copper and it may be that this is the main impurity present in solid solution. Various physical defects were presumably present also, and the difference between the measured pressure coefficients can probably be accounted for by the different contributions from impurities and strains.

## TABLE 2

T (° K)	$10^3 R_i$ ( $\Omega$ )	$\frac{10^3 R_0}{(\Omega)}$	$10^5 \frac{\mathrm{d}R_i}{\mathrm{d}T}^{\dagger}$ ( $\Omega/^\circ$ C)	$rac{T}{ ho_i}rac{\mathrm{d} ho_i}{\mathrm{d}T}$	$\frac{1}{\rho_0} \frac{\mathrm{d}\rho_0 \ddagger}{\mathrm{d}p}$ (%/1000 atm)
291.1	$42.4 \pm 2$	$18.1 \pm 2$	17.3	$1.19 \pm 0.1$	$-0.2 \pm 0.05$
80.0	$5.47 \pm 0.3$	$14.17 \pm 0.2$	15.6	$2.3 \pm 0.2$	$+0.01 \pm 0.02$
78.0	$5.15 \pm 0.3$	$14.32 \pm 0.2$			$+0.021\pm0.014$
26.5	$0.108 \pm 0.005$	$13.15 \pm 0.01$			$+0.019\pm0.005$
4.2		$15.048 \pm 0.001$			$+0.034 \pm 0.015$

 $dR_0/dT = 2.1 \pm 0.5 \times 10^{-5} \Omega/^{\circ} C$  between 26.5 and 291.1° K.

‡ We have used the following mean values of  $\frac{1}{\rho_i} \frac{d\rho_i}{dp}$  in estimating this coefficient

T (° K)	$\frac{1}{\rho_i} \frac{\mathrm{d}\rho_i}{\mathrm{d}p} (\%/1000 \text{ atm})$		
291	-0.22		
80	-0.39		
78	-0.40		

In sample III we know that the only important impurity is iron (0.056 at. %). Because the impurity resistance of this specimen is relatively large, we have been able to make some tentative deductions concerning the change with temperature of both this resistance itself and its pressure coefficient. By comparing the values of the total *resistivity* of this sample with that for ideally pure copper (i.e. we assume  $\theta_R$  is not changed for this small impurity concentration) we have deduced values of  $\rho_0$  at several temperatures (assuming always that it is meaningful to write  $\rho_{\text{total}} = \rho_i + \rho_0$ . Using these values of  $\rho_0$  and an average of the measured values of  $(1/\rho_i) d\rho_i/dp$ , we could then deduce on the same basis what should be the values of  $(1/\rho_0) d\rho_0/dp$  at these temperatures. The results of these calculations are given in table 2. We find that at 78° K the value of  $(1/\rho_0) d\rho_0/dp$  is practically unchanged from its low temperature value; whereas at room temperature, this coefficient has changed sign and its magnitude has increased ten-fold. Unfortunately, Linde reports no pressure measurements on copper + iron alloys, but a comparison with his results on gold + iron alloys shows that their pressure coefficients at room temperature (at least for the larger concentrations measured by Linde) are opposite in sign to that of this copper + iron alloy and about ten times smaller-of about the same size, in fact, as we find at the low temperatures. From the values of  $\rho_0$  at

various temperatures it appears that  $d\rho_0/dT$  is constant between 30 and 300° K and has a large positive value.\* Following Linde we have tried to correlate this coefficient with the volume change due to thermal expansion, but we find that  $d\rho_0/dT$  is about six times too large to be accounted for in this way.

It thus appears that the resistance minimum while still the most outstanding aspect of the behaviour of  $\rho_0$  is only one of many puzzling features.

#### (c) The effect of pressure on the minimum of resistance

MacDonald & Pearson (1953, 1954) found experimentally that dilute copper alloys which showed a minimum in the temperature dependence of their electrical resistance always had an anomalously high thermo-electric power at low temperatures. In discussing their results, they make use of a relation derived by Mott & Jones (1936) between the thermo-electric power, S, and the energy dependence of the electrical conductivity,  $\sigma$ ,

$$S = \frac{\pi^2 k^2 T}{3e} \left\{ \frac{\partial (\ln \sigma(E))}{\partial E} \right\}_{E=\zeta}.$$
 (2)

Here k is Boltzmann's constant, e the electronic charge, and T the absolute temperature. E is the energy of the electrons and  $\zeta$  is the Fermi energy. This is a very general formula, and, in particular, it should hold at temperatures sufficiently low that  $\rho_i \ll \rho_0$ .

MacDonald & Pearson point out that if the high thermo-electric power of these dilute copper alloys is interpreted by means of the relationship (2) the energy dependence of  $\sigma$  for these alloys must be enormous; in the present case, for example,  $\partial \ln \sigma / \partial \ln E$  would have to be larger than 100. It was therefore suggested that this remarkable effect might show itself as a strong pressure dependence of the residual resistivity of such an alloy, since by changing the volume the energy of the electrons would also be changed.

Our results show clearly that there is no such large pressure dependence. The pressure coefficient of resistance at the temperature of the minimum is the same (within the experimental error) as that at  $4\cdot2^{\circ}$  K, where the 'anomalous' component of resistance (roughly speaking, that part which is in excess of the minimum resistance) forms about 20% of the total. Moreover, these pressure coefficients are very similar in magnitude to those of samples I and II which were much purer specimens and showed no resistance minimum.

#### 6. CONCLUSIONS

It thus appears that the general behaviour of the pressure dependence of the ideal component of resistance in copper is in agreement with theoretical expectations and is governed chiefly by the effect of pressure on the lattice vibrations. On the other hand, while thermo-electric power measurements suggest a possible large pressure

406

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<sup>\*</sup> The calculated values of  $d\ln \rho_i/d\ln T$  (after correction for the temperature change of  $\rho_i$ ) agree quite well with those for pure copper. This indicates that the value we have assigned to  $d\rho_0/dT$  is approximately correct.

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## Pressure coefficient of resistivity of copper at low temperatures 407

dependence of residual resistance in an alloy showing a marked resistance minimum, we find no such effect. The variations of  $\rho_0$  with pressure and temperature found in this work are much more striking than those found by Linde from room temperature measurements only; further experimental work is needed to help in understanding their full implications.

We are grateful to Dr D. K. C. MacDonald for his encouragement and his interest in this work. We are also indebted to Mrs D. M. Rimek and Mr W. Stockdale for technical assistance, and to Dr W. B. Pearson for many helpful discussions.

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