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The electrical resistivity of niobium and niobium–zirconium alloys

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Abstract. The electrical resistivity of samples of niobium and 75% Nb 25% Zr alloy have been measured between the superconducting critical temperatures and room temperature. The temperature dependent component of the resistivity has been compared with phenomonological equations, and it is shown that phonon induced transitions between s and d bands are largely responsible for the observed resistivity. The effect of finite fluctuations of the superconducting order parameter is discussed.

1. Introduction

The electrical resistivities of transition metals are discussed in a classic paper by White and Woods (1958), where particular attention is paid to the temperature dependent component of the resistivity ρ_T at low temperatures. It is found that in many cases an approximately integral power law provides an adequate description of the resistivity data, after subtraction of the appropriate temperature independent, defect induced resistivity ρ_0. Theory predicts (see eg Wilson (1953)) the existence of three possibly significant contributions to ρ_T for nonmagnetic transition metals. Two related contributions exist due to (i) intraband scattering by phonons of electrons, occurring mainly within the s band, with the temperature dependence of the corresponding resistivity ρ_{ss} following the expression

$$\rho_{ss} \propto T^5 \theta_D^{-5} J_5(\theta_D T^{-1}) \tag{1}$$

and (ii) the scattering of electrons between the s and d bands, the equivalent resistivity ρ_{sd} being given by

$$\rho_{sd} \propto T^3 \theta_D^{-3} [J_3(\theta_D T^{-1}) - J_3(\theta_E T^{-1})]. \tag{2}$$

Here the function $J_n(x)$ is given by the transport theory integral

$$J_n(x) = \int_0^x x^n (e^x - 1)^{-1} (1 - e^{-x})^{-1} \, dx, \tag{3}$$

θ_D is the Debye temperature and θ_E is a temperature characteristic of the minimum phonon energy required to induce s–d transitions, which is no more than a fraction of θ_D in general. In the low temperature limit ($T < 0{\cdot}05\ \theta_D$) expression (1) reduces to the familiar law $\rho_{ss} \propto T^5$, whereas at higher temperatures ($T > 0{\cdot}5\ \theta_D$)$\rho_{ss} \propto T$. Within the limit $\theta_E \leqslant T < 0{\cdot}1\ \theta_D$ expression (2) reduces to the form $\rho_{sd} \propto T^3$, and at higher temperatures $\rho_{sd} \propto T$. In a recent paper Voloshinskiy and Savitskaya (1973) claim that expression (2) is correct for alloys, but should be replaced by an expression for ρ_{sd} similar to equation (1) for very pure metals. They attribute the varying results obtained by different workers for nominally pure metals to variations in the degree of sample purity. At very low temperatures equation (2) is replaced by an expression with the form $\rho_{sd} \propto exp(-\theta_E T^{-1})$. Finally a resistivity contribution $\rho_e \propto T^2$ may exist due to electron–electron scattering, expected to be dominant only either at extremely low or very high temperatures. It is important to note that the accuracy of expressions (1) and (2) is limited due to (i) the inevitable variation of θ_D as a function of temperature, and (ii) the likelihood of strong curvature existing in the electronic density of states as a function of energy for a transition metal, which influences the transition probabilities at higher temperatures. However, below a temperature of approximately 0·1 θ_D, the Debye temperature is approximately constant and band curvature effects are negligible.

The data of White and Woods have been carefully re-analysed by Colquitt (1965) to establish the relative importance of ρ_{ss}, ρ_{sd} and ρ_e in the temperature range below θ_D, and the analysis for niobium is of particular interest here. Colquitt concludes that in this case the data are adequately represented by expression (2) alone, assuming $\theta_E =$ 0·1 θ_D, with phonon intraband and electron scattering making negligible contributions to the resistivity. The analysis omits the reduction in resistance now recognized to occur at temperatures above the bulk critical temperature T_c of a superconductor, such as niobium, due to local fluctuations of the superconducting order parameter which exist naturally on the microscopic scale. A number of expressions have been proposed for the corresponding increase in conductivity $\Delta\sigma$, which is not negligible for alloys in particular. In a recent paper Hake (1969) has shown that an expression for $\Delta\sigma$ of the form

$$\Delta\sigma = 0{\cdot}037\, e^2 \hbar^{-1} (l\xi_0 \ln T T_e^{-1})^{-1/2} \tag{4}$$

is appropriate for titanium alloys. Here l and ξ_0 are the mean free path for electrons and the superconducting coherence length respectively, and e and $\hbar$ have their usual meanings. Hake has clearly demonstrated that the microstatistical fluctuations in composition inevitably present in alloys, which in principle produce a range of critical temperatures, do not noticeably influence the conductivity above the bulk critical temperature. Except in the immediate vicinity of T_c, the increase in conductivity $\Delta\sigma$ is relatively small, and it is easy to show that with this simplification the total resistivity ρ is given by

$$\rho \sim \rho_n(1 - \Delta\sigma\,\rho_n) \sim \rho_0 + \rho_T - \rho_0^2\Delta\sigma \tag{5}$$

where ρ_n is the normal state resistivity, omitting fluctuation effects. Fluctuation effects persist, in principle, up to temperatures which are several multiples of T_c, and consequently well in excess of 0·1 θ_D for superconductors like niobium alloys.

In this paper we describe the measurement and analysis of the electrical resistivities of rolled niobium and niobium–zirconium alloy strip samples between the bulk critical temperature and room temperature. In previous publications (Morton *et al* 1973, 1974) we have discussed the metallurgical constitution and the thermal conductivity behaviour below 20 K of the alloy samples. Two of these samples are nominally single phased 75% Nb 25% Zr alloy, one in as rolled condition, the other annealed and quenched from 1500°C. The three other alloy samples were quenched from 1500°C and aged for increasing periods of time at 800°C to form a matrix phase and an inclusion phase, probably containing approximately 17 and 66% of zirconium atoms respectively, resulting in greatly increased superconducting critical current densities in the mixed state. The thermal conductivity data were analysed to show that the dominant thermal energy carriers are generally phonons, with the conductivity largely limited by the electron–phonon scattering. The present work was undertaken principally to investigate further the nature of the electron–phonon scattering in the alloys, and a sample of niobium was included for comparison.

2. Experimental details

The alloy samples comprised small strips with dimensions approximately 20 × 6·4 × 0·28 mm, as described previously. The purity of the marginally smaller niobium strip is not known; however, bearing in mind the experimental uncertainty of a few per cent, largely arising due to the unfavourable geometry, the value found for the resistivity at 273 K, namely 0·146 μΩm, is quite comparable with values lying in the range 0·134–0·144 μΩm found by Westlake (1973) for commercially available niobium samples with varying interstitial impurities, indicating an interstitial impurity level lying below 500 ppm by weight for the present sample. The residual resistance ratio between 273 K and the critical temperature (ie below 10 K) was found to be approximately 20, and the sample was measured in the as rolled condition to avoid further contamination.

The samples were mounted in the variable temperature cryostat described previously and the resistance was measured with a conventional four terminal arrangement, using direct current densities of approximately 0·3 A mm^{-2}. As mentioned above, the absolute precision of the resistivity determination was limited to a few per cent by the small size of the samples. However, care was taken to maintain stable temperatures during the readings, and reversed current readings were taken for each data point in the very important low temperature region where ρ_T is small, and occasionally at higher temperatures, so the relative precision is believed to be much higher, approximately 0·01% and 0·2% for alloy and niobium samples respectively in the region of the critical temperature. The critical temperatures were determined by setting stably on the rapidly rising portion of the resistance versus temperature curve, although no particular constant fraction of the normal state resistance could be selected due to the steepness of the slopes. Temperatures in the range up to 20 K were determined from a precalibrated germanium resistor by the procedure discussed previously, and were believed to be accurate to within ±0·02 K. Temperatures above 20 K were determined from a NPL calibrated platinum resistance thermometer accurate to ±0·01 K.

3. Discussion and conclusions

The resistivity versus temperature data for all samples are summarized in figure 1 and the critical temperatures are shown in table 1. As would be anticipated, the temperature dependent contribution to the resistivity is substantially the same for each sample, the major variation in ρ reflecting changes occurring in the temperature independent contribution ρ_0. A negative curvature is evident, particularly at temperatures above 100 K, quite comparable with that found for niobium by White and Woods and, for example, by Bates and Barnard (1961) for niobium–uranium alloys. Figure 2 shows the behaviour below 23 K in more detail, where it is seen that the initial rate of rise is high, but smaller for niobium than for the alloys. We have employed a computer program using a simplex minimization procedure (Nelder and Mead 1965) to compare the possible forms of equation (5) with the data, by minimization of the sum of the squares of the deviations

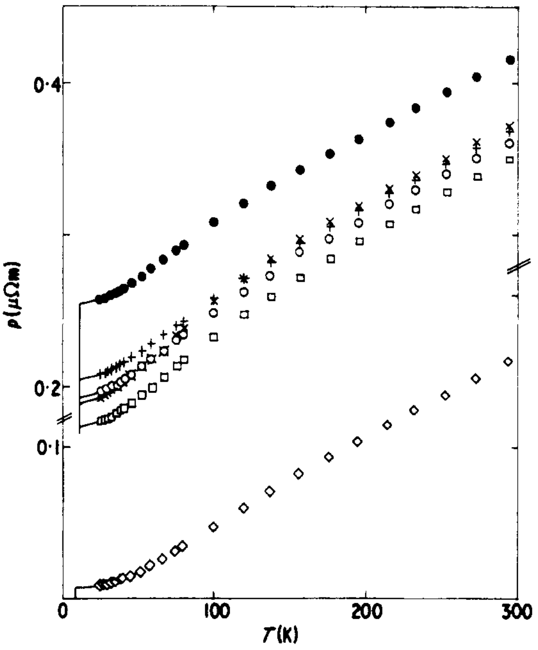

Figure 1. Variation of resistivity ρ as a function of temperature for 75% Nb 25% Zr alloys. Quenched from 1500°C, (○); as rolled, (●); aged at 800°C for 10 minutes, (×), one hour, (+), and five hours, (□); niobium, (◇).

of the experimental points from the curve, assuming for simplicity that a particular scattering mechanism is dominant. Owing to the negative curvature of the high temperature data and the anticipated temperature variation of θ_D, we have restricted this procedure to the data taken below 23 K (approximately 0·1 θ_D), where θ_D will be more constant, and equal, say, to θ_0. As a check on the numerical integration procedure a table of the transport integrals and the values at the actual data temperatures were printed out, and the values compared favourably with the tabulated values given by Colquitt.

The most apt equation was found to be

$$\rho = \rho_0 + c_1 T^3 \theta_0^{-3}[J_3(\theta_0 T^{-1}) - J_3(\theta_E T^{-1})] - c_2 \rho_0^2(\ln T T_c^{-1})^{-1/2} \qquad (6)$$

confirming s–d scattering as the dominant electron–phonon scattering mechanism. However the data are insufficiently precise to allow very accurate determinations of values for θ_0 and θ_E. When $T < 0{\cdot}1\,\theta_0$, $J_3(\theta_0 T^{-1})$ is constant to within 1%, hence the

Table 1. Critical temperatures

Sample treatment	T_c (K)	θ_0 (K)	θ_{100} (K)	ρ_0 (μΩm)	c_1 (μΩm)	c_2 (mΩ^{-1})	$(l\xi_0)^{1/2}$ (nm)
Quenched	10·71	220	194	0·193	0·367	1·47	6·2
As rolled	10·86	220	186	0·255	0·381	0·89	10·1
Aged 10 min	10·71	220	175	0·189	0·537	1·74	5·2
Aged 1 h	10·79	220	195	0·205	0·347	1·42	6·4
Aged 5 h	10·80	220	201	0·175	0·363	2·26	4·0
Nb	9·29	250	266	0·00733	0·227	0·109	~53

temperature dependence of the coefficient of T^3 in expression (6) is due largely to the temperature dependence of the $J_3(\theta_E T^{-1})$ term, and when $\theta_E \ll \theta_0$, the case found here, the latter term is relatively small, so the excellence of fit to the data is rather insensitive to variation of either θ_0 or θ_E. Hence appropriate calorimetrically determined values (taken from the papers by Morin and Maita (1963) and Hayes and Brotzen (1974)) for temperatures above 10 K were assumed, with θ_0 equal to 220 and 250 K for the alloys and niobium respectively, and a nominal small value for $\theta_E = 0{\cdot}1\ \theta_0$, after Colquitt. The corresponding smoothed curves are shown as graphs of $\rho - \rho_0$ against temperature in figure 2, and in more detail for quenched 75% Nb 25% Zr alloy and pure niobium in figures 3 and 4 respectively. It is immediately apparent that the excellence of fit could not be noticeably improved. However, it is not surprising that, as an alternative to the integral terms in expression (6), a simple T^3 relation was equally satisfactory in this temperature range, corresponding essentially to reducing θ_E to zero. The coefficients in expression (6), rounded to three significant figures, are summarized in table 1. The value of c_1 is seen to be remarkably constant for the alloys, with one exception. In this particular sample the zirconium rich phase has probably just started to precipitate as small particles, after a short ageing period; and the more rapid rate of increase of resistivity observed generally for this sample may be related to the high rate observed by White and Woods for pure zirconium, as compared with niobium. For niobium the

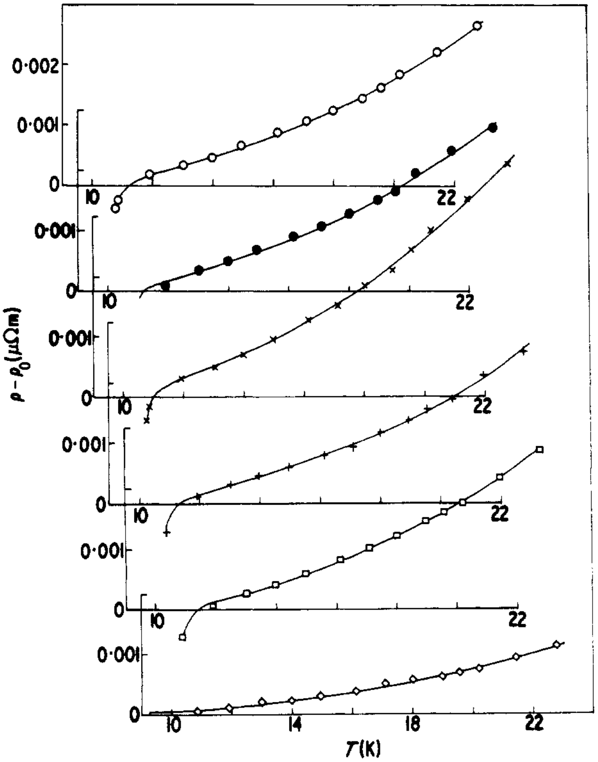

Figure 2. Variation of resistivity $\rho - \rho_0$ as a function of temperature for 75% Nb 25% Zr alloys and niobium. The curves represent the behaviour of equation (6).

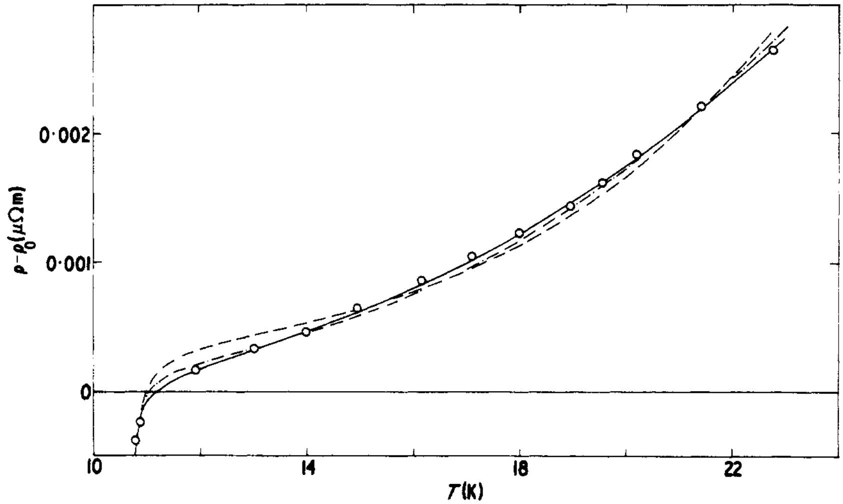

Figure 3. Variation of resistivity $\rho - \rho_0$ as a function of temperature for quenched 75% Nb 25% Zr alloy. The full curve represents the behaviour of equation (6). The broken and chained curves represent the behaviour of an equivalent expression, assuming the temperature dependence of the phonon scattering induced resistivity to follow equation (1), with θ_0 equal to 250 and 150 K respectively. Curves with intermediate values of θ_0 lie between the two curves shown.

fluctuation effects are small, and in this case $\rho - \rho_0$ is closely proportional to T^3, as shown in figure 5. An expression for ρ based on equation (1) was markedly less satisfactory, and a reasonable fit to the data is only obtained, as shown in figure 3, with θ_0 as low as 150 K, which is unrealistic. Notice that in figure 3 in this case the actual resistivity curve is shown, rather than $\rho - \rho_0$, as the value of ρ_0 is slightly different. A simple T^5 relation is strictly a less viable alternative to the full integral expression in this case, as $J_5(\theta_0 T^{-1})$ is only constant to within 8% at temperatures below 0·1 θ_0.

On inserting the coefficients in table 1 in expression (6) and extrapolating to higher temperatures it is found that the calculated resistivities are noticeably too large above

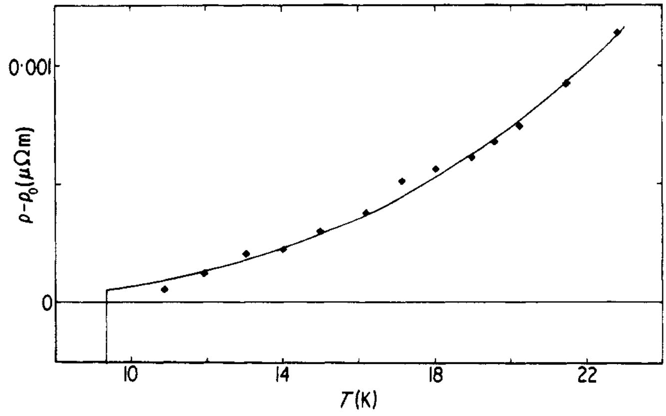

Figure 4. Variation of the resistivity $\rho - \rho_0$ as a function of temperature for niobium. The curve represents the behaviour of equation (6).

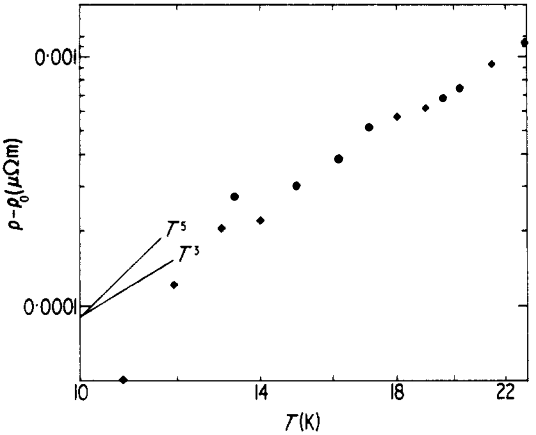

Figure 5. Variation of the resistivity $\rho - \rho_0$ as a function of temperature for niobium on a dual logarithmic plot. The lines represent simple T^3 and T^5 power law dependences.

approximately 30 K, except for niobium. Since the excellence of fit to the lower temperature data is not particularly sensitive to variations in θ_0, it follows that some effective value θ_T could be selected which would allow an approximate fit to all data up to approximately 100 K, where noticeable curvature appears. Since the value of $[J_3(\theta_T T^{-1}) - J_3(0{\cdot}1\ \theta_T T^{-1})]$ is almost independent of likely variations in θ_T at low temperature, as discussed above, any change in θ_T will produce a corresponding change in c_1, where it may be assumed to a good approximation that $c_1\ \theta_T^{-3}$ is a constant. Hence, as θ_T will not be too different from θ_0, and fluctuation effects are small at higher temperatures, it is sufficiently accurate to evaluate an effective θ_T for higher temperatures by converting $J_3(\theta_T T^{-1})$ values calculated from the expression

$$J_3(\theta_T T^{-1}) = (\rho - \rho_0)\theta_0^3\, T^{-3}\, c_1^{-1} + J_3(0{\cdot}1\ \theta_0\, T^{-1}) \qquad (7)$$

where ρ_0, c_1 and θ_0 are the low temperature values obtained previously, and ρ is the resistance at a temperature in the range up to 100 K. Values for θ_T calculated in this way at temperatures between 40 and 100 K were approximately constant, and the values for θ_{100} are shown in table 1. The procedure is, in fact, very comparable with the familiar extraction of an effective θ_D from the coefficients of expression (1) in the low and high temperature limits. A noticeable decrease is confirmed for all samples except niobium. In the latter case the initial rate of increase of resistivity is smaller (although the incremental change $\rho_{273} - \rho_0$ is comparable), so the procedure is rather less accurate. However it is entirely possible that the assumed θ_0 value of 250 K is too low. The calorimetric value at 3 K is approximately 276 K, and a value closer to this figure may be more appropriate in the range between 10 and 23 K. However, these features suggest that the behaviour of niobium may differ slightly from the alloys.

The coefficient c_2 of the increase in conductivity due to fluctuation effects remains approximately constant for the alloys, but is much smaller for niobium, as anticipated, and the value must be regarded as very approximate in this case. The resistivity varies rapidly as a function of temperature close to T_c, where expression (4) may be replaced by the approximate form with $\Delta\sigma$ proportional $(T - T_c)^{-1/2}$. Correspondingly, errors in the value of $(T - T_c)$ may lead to disproportionately large differences between the observed and calculated resistivities, and since minimizing these differences improves the criterion of excellence of curve fitting, large variations in the value of c_2 may result from a rather small change in the value of T_c, say. It is more satisfactory, therefore, to place greater reliance upon data points for which $(T - T_c)$ is not too small, particularly if the transition is extremely sharp, as is the case for niobium. It is worthwhile to note that, as fluctuation effects are relatively small at temperatures in the region of 20 K, it is unlikely that adopting any alternative expression for $\Delta\sigma$ would result in changes in the form of ρ_T. The values of $(l\xi_0)^{1/2}$ calculated from expression (4) are shown in table 1, and are very similar to those found for titanium alloys by Hake. Evidently microfluctuations in composition have relatively small effects on the data and the subsequent analysis; however, as the second-phase inclusions in the aged alloys have critical temperatures slightly below that of the matrix phase, the measured critical temperatures should correspond to the matrix.

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