Low Temperature Resistivity and Thermopower Anomalies in Pure Gold

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Minute quantities of magnetic impurities, particularly iron, can change the low temperature transport properties of gold beyond recognition. Careful measurements of the resistivity and thermopower can yield a valuable insight into the type of impurity present. It has been possible to remove iron selectively by a high temperature chlorine treatment, and remanent iron concentrations as low as 1 part per billion (10^{-9}) have been obtained.

Any pure metal has a low temperature resistivity that does not change with temperature, the so-called "residual resistivity" ρ_0. Figure 1 shows the approach to this value. ρ_0 depends on the physical and chemical perfection of the metal: it is increased by strain, dislocations, vacancies, interstitials and by foreign atoms, i.e. chemical impurities.

A measurement of the "resistance ratio"

$$R = \rho_{293K}/\rho_{4K}$$

furnishes a simple and convenient test of the state of a metal sample. A standard polycrystalline piece of gold will show a resistance ratio between 30 and 300. A piece of "Spec-pure" gold will on occasions yield a value of 800. To obtain R>1000 one must generally go to carefully annealed single crystal specimens (1).

Very often the resistivity exhibits a minimum at low temperatures (see Figure 1), with an increase at the low temperature end. This curious state of affairs had been discovered in the 1930s, but only recently has a proper explanation been given by Kondo (2). In all cases where a resistance minimum was found, there were also anomalies in the thermopower, magnetoresistance and magnetic susceptibility, as reported by Berman and Kopp (3, 4). This latter fact, and the removal of most of the anomalies after

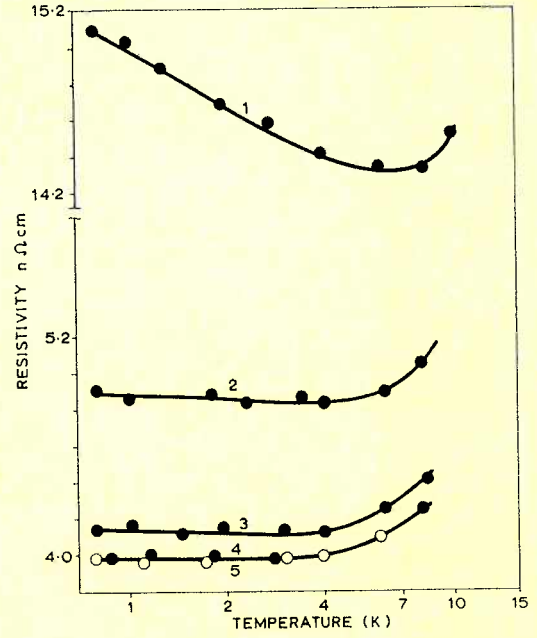

Fig. 1 Resistivity of Au-Fe specimens containing various amounts of iron (1 very impure, 5 very pure)

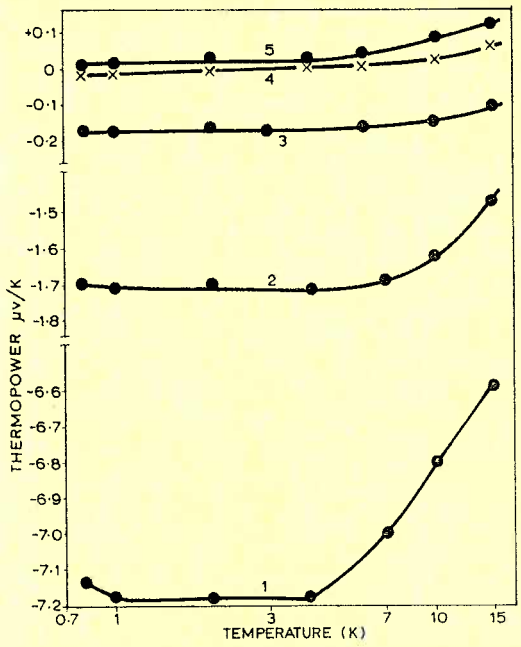

Fig. 2 Thermopower of Au-Fe specimens containing various amounts of iron (1 very impure, 5 very pure)

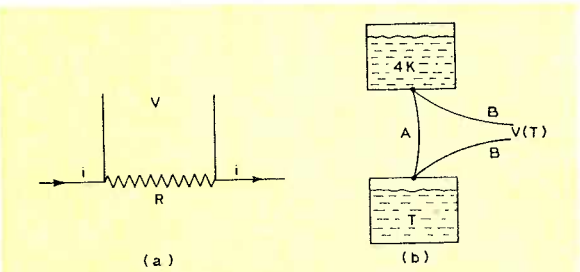

Fig. 3 Experimental methods of transport property measurements at low temperatures

(a) Resistivity

(b) Thermopower (A=active part, B=passive part of thermocouple)

oxidation, led to the identification of magnetic impurities, chiefly iron, as the cause of the anomalies. Very small amounts of these impurities are sufficient to mask completely the normal behaviour; thus 1 p.p.m. of iron will make the thermopower of pure gold change sign, as shown in Figure 2.

A pure noble metal has a thermopower that is (i) small, (ii) positive and (iii) linear in temperature below 10 K. With the addition of a few p.p.m. of magnetic impurities, this becomes (i) anomalously large, (ii) negative and (iii) temperature independent between 1 and 10 K. The change in magnitude at 4 K may be as large as a factor of 1000. Only in semiconductors can such a small impurity concentration lend to such startling changes!

The Measurement of Transport Properties at Low Temperatures

To obtain the resistance ratio it is sufficient to measure the voltage across a current carrying sample at room temperature (~293 K) and in liquid helium (~4 K). (Simply insert the sample down the neck of a transport dewar full of liquid helium!) To obtain the resistivity and thermopower as a function of temperature is somewhat more involved. One generally uses a cryostat in which the temperature can be changed, controlled and measured by pumping on a bath of liquid helium. The vapour pressure falls rapidly with temperature, and the range 1 to 4 K is easily covered. For higher temperatures one uses a heater controlled by a feedback system. Temperature stability is possible to $\pm 10^{-3}$ K.

Figure 3 shows the principles of measurement. In Figure 3 (a) resistance is measured with a standard four probe network. Since the resistivity is extremely small at such temperatures, the voltage sensitivity must be high, say $\pm 10^{-8}$ V. This is easily achieved with a Keithley nanovoltmeter or a SQUID. It is important to make corrections for error voltages in the leads, the so-called "thermals", which can be of order 10^{-6} V. This is most easily done by reversing the current.

In Figure 3 (b) the principle of thermopower measurement is shown. One actually measures the thermal e.m.f. between two dissimilar junctions, one at 4 K and the other at a variable temperature. The thermopower is obtained from the e.m.f. by differentiation, thus

$$S(T) = dV(T)/dT$$

If the "passive" arms of the thermocouple consist of a superconductor, V (T) will refer to the sample only and no correction is necessary.

The Removal of Iron from Gold

The anomalies tend to disappear when the impurities are oxidised. However, the presence of the oxide particles presents new, uncertain sources of scattering and it would be advantageous to remove the magnetic impurities completely. In the Au–Fe system this is possible with a chlorine treatment at elevated temperatures (5), illustrated in Figure 4. The iron diffuses to the surface, combines with chlorine and leaves as a volatile chloride. If the temperature is not too high, the gold is not affected. At 800°C wires of diameter 0.1 mm thus treated have their iron concentration halved in about 2 hours.

The fall-off in concentration is exponential, in accordance with diffusion theory (6). For a cylinder of radius r and initial concentration c_0 the mean concentration after time t will be given by

$$\bar{c} \simeq 0\ 69\ c_0 \exp(-5.8\ Dt/r^2)$$

where D is the diffusion coefficient of iron in gold. At 800°C this is of order 4×10^{-10} cm^2/s (5, 7). The initial decrease in $\bar{c}$ is somewhat faster than that indicated by the equation, but after 4 hours there is good agreement. Figure 5 shows that the concentration has been reduced from 13 p.p.m. to practically zero in 16 hours.

The Measurement of Extremely Dilute Concentrations of Iron in Gold

Above 1 p.p.m. standard chemical techniques can be used to determine the iron concentration. This

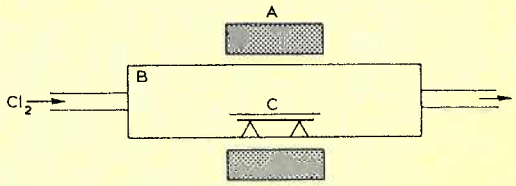

Fig. 4 The use of chlorine gas to remove iron impurities from gold

A=furnace at ~800°C

B=quartz tube through which chlorine is flowing at ~1 torr

C=specimen in open "Spec-pure" silica tube

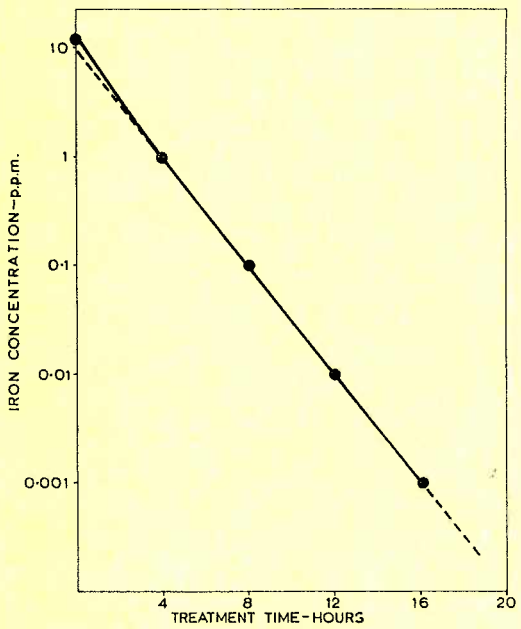

Fig. 5 Iron concentration is a function of chlorine treatment time. The initial concentration is 13 p.p.m.

unfortunately is no longer true below 1 p.p.m. so that we must use the anomalies themselves. The residual resistivity is not a very sensitive tool, since it includes all types of scattering outlined above and the effects of a few parts per billion of iron will not show up. Fortunately the thermopower is different: the Nordheimer-Gorter rule states that for two scattering mechanisms, the thermopower is (8)

$$S=(S_1\rho_1 + S_2\rho_2)/(\rho_1 + \rho_2)$$

If 1 refers to magnetic scattering and 2 to all other processes, then theory (9) gives

$$S_2 \simeq 3\times10^{-2}\mu V/K \text{ at } 4\ K$$

$$\text{while } S_1 \simeq 20\ \mu V/K$$

and for Au–Fe this reduces to

$$S \simeq 8\ c/\rho\ \mu V/K$$

where c is in p.p.m. and ρ in nΩ cm

The following table applies to actual measurements made by the writer (7):

	Thermopower μ(V/K)		
c(p.p.m.)	T=1 K	T=4 K	T=10 K
10	−5.5	−5.5	−5.2
1	−1.7	−1.7	−1.6
0.1	−0.18	−0.17	−0.14
0.01	−0.01	−0.01	+0.03

As this table indicates, the thermopower is almost temperature independent except for a slight reduction at higher temperatures. A simple measurement of S and ρ will give c, at least in the range from 0.01 to 10 p.p.m. Below 0.01 p.p.m. it becomes very difficult to pick up the effects of the iron. This is not surprising since the mean distance between the impurities is about 400 lattice spacings. Above 10 p.p.m. the ordinary methods of analysis are sufficient.

Conclusions

Magnetic impurities behave differently from other defects in metals like gold. They are able to influence electronic properties down to the part per billion level. These changes themselves can be used to determine the impurity concentration below 10 p.p.m. where chemical methods begin to fail. The thermopower is not too difficult to measure and affords the best means of testing for such impurities. It is possible, in the case of gold, to remove the iron selectively by a treatment with chlorine. In this way the iron concentration of a single specimen may be progressively reduced to a very low level.

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A Dossier on Gold

The latest in a series of Mineral Dossiers—reports on minerals of economic importance to Great Britain—is concerned with gold. Compiled by Dr R. S. Collins of the Institute of Geological Sciences, it assembles information not normally brought together and covers a wide range of interests, starting with the properties of gold and its mineralogy and mode of occurrence with particular reference to the small resources of gold in the United Kingdom.

A section on the uses of gold briefly surveys its applications in the textile industry, in the decoration of glass and ceramics, and in electrical and electronic engineering, while the usage of gold alloys in high temperature brazing in the aerospace industry and in the insulation of glass windows are also covered.

There is a well-informed section on the history of gold and its many uses in antiquity, followed by a statistical survey of the price of gold and its production and a summary of legislation on its ownership, sale and use from ancient times until the present day. A detailed bibliography is also included.

Mineral Dossier 14, "Gold", published by Her Majesty's Stationery Office, is available at £1·25.