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The effect of pressure and temperature on the electrical resistance of rubidium and caesium

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Measurements have been made of the electrical resistivity of rubidium and caesium at temperatures between 1.5 and 300 °K and at pressures up to 3000 atm. From our results we have calculated the ideal resistivity and its pressure derivative both at constant pressure and at constant density. The results are compared with those of the lighter alkali metals and with theoretical predictions.

1. Introduction

In an earlier paper (Dugdale & Gugan 1962)† the effect of pressure on the electrical resistance of lithium, sodium and potassium at low temperatures was described. In this paper we present comparable results on rubidium and caesium. In this way we are able to compare the resistivity of all the alkali metals from low temperatures (ca. 2 °K) up to room temperature both at constant pressure (effectively zero) and at constant volume. In addition, we are able to compare the volume coefficients of resistivity and their dependence on temperature for the whole series of alkali metals.

Except for Bridgman's work and that described in I, most of the previous experiments on the resistivity of alkali metals have been done on specimens contained in capillary tubes. In the present series of experiments bare wires were used since these are essential if accurate measurements under pressure are to be made. As Bridgman (1925) has pointed out and as our earlier experience on the lighter alkali metals (Dugdale & Gugan 1963) showed, even for measurements of the temperature dependence of resistivity capillary specimens are unsatisfactory. This is particularly true of rubidium and caesium. Indeed, the thermal contraction of caesium is so large relative to glass that in some of the previous experiments in which glass capillaries were used the results showed very marked anomalies and in extreme cases the specimens became open circuit during cooling or heating. In rubidium, too, the anomaly originally found by MacDonald (1952) is almost certainly to be ascribed to the fact that the specimens were contained in glass capillaries.

In I it was pointed out that the present theory of electrical resistivity could not account for the volume dependence of the electrical resistivity of any of the metals discussed there. In particular, it was emphasized that even for sodium and potassium which appear to approximate well to the free electron model of a metal the theory was unsatisfactory. Since then there have been new theoretical

† In what follows we shall refer to this paper as I.

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calculations which agree rather well with experiment for these two metals and these calculations will be referred to later when we discuss our results on rubidium and caesium.

2. EXPERIMENTAL

The experimental techniques of measurement were essentially similar to those already described or referred to in I. Measurements were made of the resistance of the specimens as a function of temperature between ca. 2 and 300 °K at effectively zero pressure. In a second apparatus the pressure dependence was measured in a similar temperature range. The pressure transmitting medium was helium: in its fluid form at the higher temperatures and in the solid phase at the lowest temperatures. The pressure range was up to 3000 atm.

The main differences from the earlier experimental techniques were in the preparation and mounting of the specimens. Because rubidium and caesium, particularly the latter, are highly reactive metals which ignite spontaneously in a humid atmosphere the handling of the specimens had to be carried out either in a vacuum or in a dry box with an inert gas atmosphere.

The specimens consisted of wires about 40 cm long and 1 mm in diameter wound on a former similar to that described by Dugdale & Gugan (1960). The metal was removed from its original glass capsule and melted into an extruding cell under vacuum of the order of 10^{-5} to 10^{-6} mmHg. The cell was then transferred into a stainless steel dry box of the conventional type, filled with clean dry helium. The metal wire was extruded into dry transformer oil, at about -5 °C, under which it was wound onto the former; the former was then mounted on the apparatus, the excess oil brushed off with a fine artist's brush and the high pressure vessel screwed on. The whole was then transferred from the dry box to the cryostat, the high pressure connexions were made and the cryostat was then filled with liquid nitrogen.

During the experiments we had some trouble with oxidation of the specimens. In general high pressures seem to inhibit this effect and we found it safest at temperatures above about 180 °K to keep a pressure of at least 100 atm on the specimens in the high pressure apparatus. This was also experimentally convenient although it had the disadvantage that we had to obtain the zero pressure value of the resistance for each pressure run by extrapolation. In one of our experiments on caesium near room temperature we found the 'transition' reported by Bridgman (1923) which occurs when a specimen becomes appreciably oxidized. This shows up as a step in the resistivity-pressure curve at temperatures near 0 °C and is presumably related to the change with pressure of the eutectic temperature of the caesium oxide-caesium metal system. If the specimen is not contaminated, a smooth dependence of resistance on pressure is found with only slight effects due to oxidation.

In the low pressure apparatus we had similar problems. At temperatures above 140 °K in the case of rubidium (specimen 4) and 180 °K in the case of caesium (specimen 2) we found that the resistance of the specimen increased slowly while the temperature was kept constant. We attributed this to oxidation at the surface