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## LETTER TO THE EDITOR

### Impurity quenching effects in potassium

D Gugan, R T L Lim and G M Meaden

H H Wills Physics Laboratory, University of Bristol, Bristol, UK

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**Abstract.** Large, reversible, and reproducible changes of residual resistivity have been observed in rather pure potassium as a result of temperature cycling between 255 K and the liquid state. The excess resistivity can be annealed from  $\rho_0 \approx 80 \text{ n}\Omega \text{ cm}$  to  $\rho_0 \approx 8 \text{ n}\Omega \text{ cm}$  with a time constant of about an hour. Solution and dissolution of impurities appear to be involved. Some uses for the phenomenon are suggested.

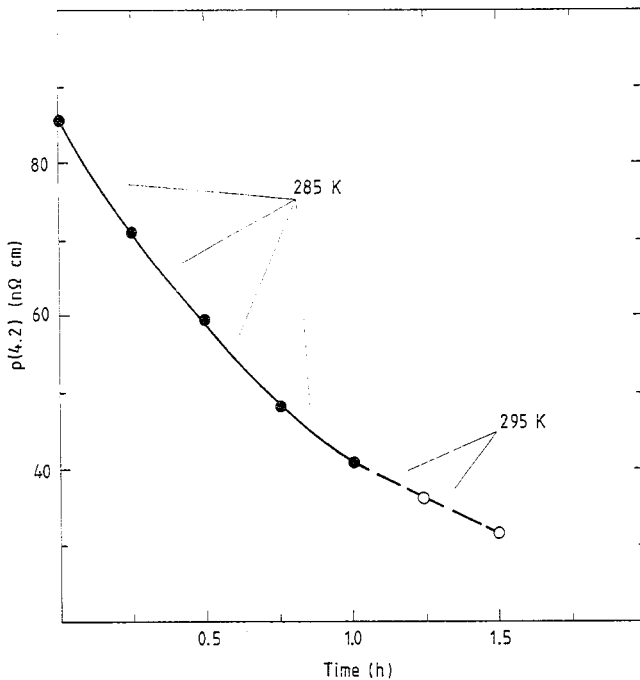
Large variations in the residual resistivity of nominally pure potassium as a result of different cooling procedures have been reported several times over the last twenty years, with perhaps the most spectacular result being the increase from 1.42 to 18.6 n $\Omega$  cm seen by van Kempen *et al* (1981). These variations are usually described as being due to quenching (although very rapid timescales are never involved), and were originally usually ascribed to the results of physical damage, including the generation of dislocations. It has been shown by Bishop and Overhauser (1981) and by Gugan (1982) that these explanations are untenable since they involve numerical discrepancies of several orders of magnitude, but the origin of the variations has not been studied systematically and remains obscure.

In some recent work on the compressibility of potassium using a non-contacting, eddy current technique, very large increases of residual resistivity,  $\rho_0$ , were observed in potassium that had been melted shortly before extrusion into cylindrical samples, and it was confirmed that this was not an artefact of the measurement technique since DC measurements on extruded wires gave similar results<sup>†</sup>: a typical increase of  $\rho_0$  was from 5 to 30 n $\Omega$  cm in both of these experiments. The temperature range of interest was near to room temperature, so to allow a systematic study of thermal cycling, samples were made by vacuum casting potassium from the same stock into pyrex tubes of 1.4 mm internal diameter.  $\rho_0$  was measured from the asymptotic high-frequency response of the samples in a modified Hartshorn bridge, as described by Loveday and Gugan (1988), the uncertainty in  $\rho_0$  being less than  $\frac{1}{2}\%$ . Casting alkali metals in glass is known to have an effect on the temperature dependence of sample properties because of strains arising from differential thermal expansion (Dugdale and Gugan 1963), but these are only at the level of about 1% of  $\rho_0$ , which is much less than the changes we shall discuss.

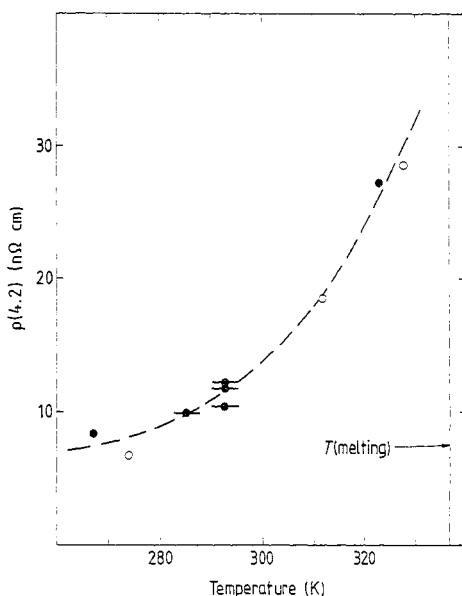
<sup>†</sup> We are grateful to Messrs A P Howes and J Ryder for carrying out these experiments as part of an undergraduate project.

Six separate runs starting from the melt at  $\approx 100^\circ\text{C}$  were made on the same cast potassium specimen, and 34 measurements were made of  $\rho_0$  after a variety of controlled time and temperature annealing treatments; in practice, all the measurements were made at the normal boiling point of helium, but since the temperature-dependent contribution at 4.2 K is only about  $0.28\text{ n}\Omega\text{ cm}$  (Gugan 1971), the difference between  $\rho_0$  and  $\rho(4.2)$  is not significant here. For samples cooled from the melt to 77 K within a few minutes,  $\rho(4.2)$  varied between 60 and  $86\text{ n}\Omega\text{ cm}$ , while after the samples were annealed near to room temperature for periods between one and nine days the resistivities fell to between  $8.3$  and  $12.0\text{ n}\Omega\text{ cm}$ . These values of  $\rho(4.2)$  for the annealed samples are about twice as high as before encapsulation, which would indicate that some contamination has occurred, but the annealed residual resistivity corresponds to concentrations of only about  $10^{-2}$  at. % impurity in solid solution, i.e. to only about ten times worse than the lowest values that have been reported (see, e.g. Gugan 1971), so these samples are in the range that would usually be regarded as of high purity. Some subsequent check measurements on a second specimen encapsulated in the same way as the first gave even larger changes of  $\rho(4.2)$ : from  $241\text{ n}\Omega\text{ cm}$  after rapid cooling from the melt, falling to  $10.7\text{ n}\Omega\text{ cm}$  after two days at room temperature.

The excess resistivity observed after cooling from the melt did not begin to fall until the annealing temperature reached 255 K, above which recovery occurred with a time constant of typically about one hour. The slope-change method for estimating activation energies from a combination of isochronal and isothermal anneals (Damask and Dienes 1963) gave the results shown in figure 1. The rate of recovery at 285 K is close to exponential (assuming an asymptotic value of  $10\text{ n}\Omega\text{ cm}$  for  $\rho(4.2)$ ) with a time constant of about 1.1 h, but the change of slope between the two isotherms is unexpected since



**Figure 1.** Isochronal recovery curves for potassium measured at 4.2 K after cooling from the melt and then annealing at 285 and 295 K. The experimental uncertainty in  $\rho$  is about  $\frac{1}{2}\%$ .



**Figure 2.** The resistivity at 4.2 K,  $\rho(4.2)$ , for samples allowed to equilibrate for more than 24 h at the temperatures shown, and then cooled to temperatures where no recovery occurs. The experimental uncertainty in  $\rho$  is about  $\frac{1}{2}\%$ . The broken curve is an exponential fit (see text). Full circles, March 1988; open circles, August 1988.

the rate of recovery is *less* at the higher temperature. An obvious explanation of this apparent anomaly is that the fully recovered states are not the same for the two temperatures, i.e. that the asymptotic value of  $\rho(4.2)$  is *higher* at 295 K than at 285 K. Since the time constant is long compared with practicable sample-temperature cycling times it is easy to test this directly, and figure 2 shows values of  $\rho(4.2)$  for samples that were allowed to equilibrate for more than 24 h at temperatures between 267 and 323 K and then cooled quickly (within a few minutes) to temperatures where no recovery occurs (the points near to 290 K were not measured under strictly controlled conditions, but are estimates of the sample temperature over the 24 h prior to measurement). The measurements show an unmistakable rise as the temperature approaches the melting point, while some subsequent check points on the same specimen (figure 2, open circles) differ somewhat at the lowest temperature but clearly show the same general behaviour.

These results show that rather pure samples of potassium can indeed display very large charges of residual resistivity on thermal cycling, and it is reasonable to suppose that the recovery process of figure 1 and the quenching process of figure 2 result from the same mechanism. Whether this is the same phenomenon as has been previously reported for other samples is impossible to confirm, but it seems not improbable. Physical defects such as dislocations, vacancies, and interstitials have already been shown to be untenable as explanations for these quenching effects (Gugan 1982) on account of the magnitudes of the changes observed, and this is true, *a fortiori*, for the present results; also, an additional and stronger argument against physical defects comes from the temperature range for recovery observed here, above 255 K, which is about 100 K above even the highest recovery stage observed by Gurney and Gugan (1971) in a systematic study of defect annealing after cold working in samples of potassium of various degrees of purity. If one accepts this argument, the only realistic source of the extra scattering is

chemical impurities that are moving into or out of solid solution. What these impurities are we do not know. One would expect sodium to be the major impurity, but it is known from the work of MacDonald *et al* (1956) that the KNa system has a eutectic at 261 K with a terminal solubility limit of about 4.5 at. % Na, far higher than the impurity levels operating here. Apart from that for sodium, there appears to be no published phase diagram that shows a limited region of solid solubility in potassium; either there is complete miscibility as for rubidium and caesium or, allegedly, no solubility. This latter cannot be strictly true, of course, and it may be that the operative impurity has a reaction isotherm very close in temperature to the melting point of potassium and a very small range of solid solubility: the potassium–bismuth system is an example of such behaviour (see, e.g., Vol 1967).

Models for alloy behaviour (see, e.g., Cottrell 1955) predict that the solubility in terminal solid solution,  $c$ , for a binary alloy should obey

$$c = \exp(\Delta S/k) \exp(-\theta/T) \quad (1)$$

where  $c$  is the mole fraction,  $\Delta S/k$  is a vibrational entropy factor arising from strain fields around the solute, and  $\theta$  is a characteristic temperature corresponding to the enthalpy of solution,  $\theta \equiv \Delta H/k$ . The data of figure 2 are not adequate for a precise fit to this expression, but the broken curve shows a tentative fit,

$$\rho(4.2) = [6 + 4.7 \times 10^6 \exp(-4000/T)] \text{ n}\Omega \text{ cm} \quad (2)$$

and if we *assume* a typical impurity resistivity of  $1 \mu\Omega \text{ cm/at. \%}$  for the exponential part, we obtain

$$c(\text{impurity}) = 47 \exp(-4000/T). \quad (3)$$

The value of 47 for the pre-exponential part of equation (3), corresponding to  $\Delta S/k = 3.85$ , compares with values ranging between about 10 and 60 observed for impurities in aluminium (see, e.g., Cottrell 1955), but the value of  $\theta = 4000 \text{ K}$ , corresponding to  $\Delta H = 0.34 \text{ eV/atom}$  ( $7.9 \text{ kcal mol}^{-1}$ ) is extremely high compared with the (very limited) information on heats of solution in alkali metals and is similar in size to the enthalpies of formation of some of the known compounds of potassium (see, e.g., data given by Kubaschewski and Catterall (1956) and Ohse (1985)), perhaps indicating the formation of bonded electron-scattering impurity sites.

If we assume that the time constant being about one hour is due to chemical impurities coming out of solution and diffusing to grain boundaries, we can use the self-diffusion coefficient of potassium measured by Mundy *et al* (1971), together with the fact that the activation energy for impurity diffusion is (usually) not much different from that for self-diffusion (Le Claire 1964) to estimate the range of the diffusion. Some model is necessary, and assuming that randomly distributed impurities diffuse to spherical sinks of radius  $R$  then, as shown in Damask and Dienes (1963), the annealing progresses as exponential decay with time constant,  $\tau$ , given by  $\tau = R^2/\pi^2 D$ , where  $D$  is the diffusion coefficient at the temperature considered. With  $\tau$  measured to be about 4000 s and  $D$  about  $10^{-8} \text{ cm}^2 \text{ s}^{-1}$  at room temperature,  $R$  proves to be about 0.2 mm. This certainly indicates long-range migration, and it is reasonably compatible with impurity diffusion to grain boundaries since the grain size in alkali metal wires is usually about the size of the diameter, here 1.4 mm. The calculated range is close to its absolute upper limit which implies that the activation energy for the diffusing species *cannot* be much different from that for the monovacancy: if a vacancy–impurity aggregate of some sort is involved, then the binding energy must be rather low, probably less than 0.05 eV, which seems

anomalous compared with the value of 0.35 eV previously estimated for  $\Delta H$  using equation (1).

The present results, although preliminary and limited, show unequivocally that quenching effects can be very large in potassium, and also that the timescales are such that it would be possible to study them in considerable detail. Full interpretation is likely to depend on the metallurgy of the samples used, in ways possibly not easy to characterise, and in this context it is significant that MacDonald (1955), in an attempt to freeze in vacancies, performed quenching experiments on *sodium* of purity comparable with our potassium without ever seeing changes of more than 5% of  $\rho_0$ : it is now known that no conceivable quenching rate could freeze vacancies into the alkali metals, but the two orders of magnitude difference in the impurity quenching effects in sodium and potassium is remarkable. Notwithstanding these difficulties, our results lead to the important practical conclusion that there is a simple way to control the residual impurity scattering in potassium which could be valuable in low-temperature transport experiments including, e.g., (i) the study of deviations from Matthiessen's rule in potassium (see Bobel *et al* 1976), which has implications for the charge-density-wave model of the ground state of potassium (see, e.g., Overhauser (1985), § 4.11) but for which the evidence is unconvincing at present; (ii) the study of the anomalous, sample-dependent,  $T^2$  term in the electrical resistivity of potassium below about 1 K, where control of the impurity scattering at a very low level could help discriminate between alternative theoretical models (see, e.g., Overhauser (1985), § 4.9; Kaveh and Wiser (1982)); and (iii) the study of defect distributions by de Haas-van Alphen measurements, where annealing near 250 K has been observed to have a major effect on the dependence of DHVA amplitude on crystal orientation (O'Shea and Springford 1983): controlled impurity quenching could be a useful tool in all such experiments.

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