Lattice Defects and the Electrical Resistivity of Metals

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CONTENTS

§ 1. Introduction

It has long been known that the electrical resistivity of a metal is a property which is sensitive to changes of structure brought about by cold-working. In principle, therefore, a study of resistance changes during deformation and during annealing is capable of yielding information about the structure of plastically deformed metals, but until recently it has been impossible to relate changes of resistivity with any certainty to specific lattice defects such as vacancies, interstitial ions and dislocations. Recent advances have come about mainly through the employment of recovery experiments which have been designed to reveal differences in the mobility of several types of lattice defects and so to lead to their identification. Further, two new techniques have been developed by which it has been possible to create particular types of lattice defects, so that their effect on resistivity can be studied more or less without the complication of the presence of appreciable concentrations of other defects. The first of these consists in quenching a metal from a high temperature and attempting to freeze-in defects such as vacancies which are present in greater concentrations at high temperatures than at low. The second type of experiment consists in subjecting a metal to irradiation by electrons, neutrons, protons, deuterons or other particles, so that by collisions within the lattice, vacancies and interstitial ions are created as primary defects. We shall first summarize calculations of the effect of lattice defects on resistivity and then discuss the results obtained in the three main types of experiment—quenching, irradiation, and deformation.

An early version of this review formed the basis of an introductory paper given at a recent informal conference on *Lattice Defects and the Electrical Resistivity of Metals* (Broom 1953). I am grateful to all the participants in that conference who have stimulated and made possible the preparation of this article.

§ 2. Theory

The primary theoretical problem is the calculation of the effect on electrical resistivity of various lattice defects. The secondary problem of the estimation of the mobility of various defects will be discussed in § 2.2.

2.1. *The Effect of Defects on Resistivity*

2.1.1. *Vacancies*

A calculation has been made by Dexter (1952 b) using a Thomas–Fermi method to determine the effect of point singularities on resistivity. His result for copper, silver and gold was that one atomic per cent of vacancies would give an increase of resistivity of $\sim 0{\cdot}4\,\mu\Omega$cm.

Jongenburger (1953) has pointed out an error in Dexter's approach and by a different method has found that vacancies have an appreciably greater effect on resistivity, namely $1{\cdot}3\,\mu\Omega$cm per atomic per cent of vacancies in copper. No explicit calculations have been made for pairs of vacancies or for groups of three or more, but Seitz (1952 a) has indicated

that the aggregation of single vacancies will lead to a fall in resistivity. No explicit comparisons with experiment have yet been possible.

2.1.2. *Interstitial Ions*

The only estimate is due to Dexter (1952 b) who found that one atomic per cent would increase the resistivity of copper, silver or gold by $\sim 0{\cdot}6\,\mu\Omega$cm.

2.1.3. *Dislocations*

Several accounts of the resistivity due to dislocations have been published, notably by Koehler (1949), Mackenzie and Sondheimer (1949), Landauer (1951), Hirone and Adachi (1951), and by Dexter (1952 a). These have been criticized by Hunter and Nabarro (1953) who have given new results of their own. In accord with previous calculations, marked anisotropy of scattering by a single edge dislocation is found. There is no resistance in the direction of the dislocation axis and the resistance in the slip direction is one third that in the direction at right angles to the slip plane. For a screw dislocation there is again no resistance parallel to the axis, but scattering in directions perpendicular to the axis is isotropic.

Although there is evidence of anisotropy of resistivity in heavily worked metals (§ 5.6), the effect is so small that for comparison of theory with experiment it is justifiable to consider a random arrangement of dislocations. The following results (Hunter and Nabarro) refer to *isotropic* increases in resistivity due to N dislocation lines per sq. cm, randomly oriented.

Copper, edge dislocations $\Delta\rho_E = 0{\cdot}59\times10^{-14}N\,\mu\Omega$cm,
screw dislocations $\Delta\rho_S = 0{\cdot}18\times10^{-14}N\,\mu\Omega$cm.
Sodium, edge dislocations $\Delta\rho_E = 2{\cdot}10\times10^{-14}N\,\mu\Omega$cm,
screw dislocations $\Delta\rho_S = 0{\cdot}18\times10^{-14}N\,\mu\Omega$cm.

Further, in the case of copper, if we assume equal densities of edge and screw dislocations, we have $\Delta\rho = 0{\cdot}39\times10^{-14}N\,\mu\Omega$cm. If we allow that up to one half of the total increase in resistivity produced in copper by cold working at room temperature may be due to vacancies and interstitials, we find $N = 5\times10^{12}$ lines/cm^2 for $\Delta\rho = 0{\cdot}02\,\mu\Omega$cm. Previous estimates of N for this increase in resistivity range from 5×10^{11} (Koehler) to 7×10^{12} (Dexter).

All recent estimates of N from resistivity data are an order of magnitude higher than those deduced in other ways (§ 5.1.2), possibly because of the neglect of two aspects of the problem in the resistivity calculations. First, although the observed increase in resistivity is almost isotropic it is very probable that dislocations are *not* arranged completely at random. So far it has not been possible to calculate the resistivity due to special groups of dislocations such as ' pile-ups ' which are thought to be present in work-hardened metals (Mott 1952). Second, the calculations take no account of dissociation of dislocations, in close-packed metals, into partial dislocations separated by a region of faulty stacking.

A crude estimate of scattering from stacking faults has been given by Klemens (1953) and it may be comparable with pure dislocation scattering. This view receives support from the discrepancy between the calculations of Hunter and Nabarro and the density of dislocations estimated in other ways, and more directly, from experimental evidence on alloys discussed in § 5.3.2.

2.2. *The Mobility of Defects*

In practice it is seldom possible to study metals containing only one type of defect, so that it is desirable to perform experiments which will lead to the discrimination of various types of defect when they are present together. This is usually achieved by determining activation energies for recovery of resistivity and then comparing the results with theoretical estimates of the mobility of simple and complex types of lattice defects.

2.2.1. *Vacancies*

In evaluating activation energies for possible diffusion processes in metals Huntington and Seitz (1942) and Huntington (1942) found the activation energy for movement of a single vacancy in copper to be about 1 ev. Seitz (1952 a) has suggested that movement of a pair of vacancies may require a lower activation energy because of the lower closed-shell interaction when an atom exchanges with one component of a pair. An explicit calculation by Bartlett and Dienes (1953) has confirmed this, showing that diffusion of a vacancy pair would require rather less than half the activation energy necessary for diffusion of a single vacancy. They also estimated that the energy required to dissociate a vacancy pair in copper lies between 0·25 and 0·59 ev, and hence it is clear that some association of single vacancies will occur if they are present in a lattice in excess of the equilibrium concentration and have sufficient mobility to approach each other.

No calculations have been carried out for groups of three or more vacancies, but large groups would probably be comparatively immobile. It would be interesting to know how a fourth vacancy would add on to a group of three ; if a planar group is built up there is the possibility, in face-centred cubic metals, of the generation of a stacking fault and a sessile dislocation (Seitz 1950 a).

2.2.2. *Interstitial Ions*

Two distinct processes seem possible for the movement of interstitial ions. In the first, an ion diffuses through the lattice, moving from one interstitial site to another, retaining its interstitial identity. In the second, an interstitial ion moves on to a normal lattice site, pushing the original occupant into a neighbouring interstitial position. Huntington and Seitz (1942) have considered that diffusion by the second process (interstitialcy diffusion) should have the lower activation energy, and have found this to be about 10 ev. As a major part of this energy is required for the formation of an interstitial ion, it is likely that movement of an

interstitial ion could take place with an activation energy of the same magnitude as that for a vacancy. In contrast to the case of diffusion of vacancy pairs, interstitial pairs (if stable) would be much less mobile than single interstitial ions (Seitz 1952 a).

2.2.3. *Dislocations*

It is not easily possible or indeed profitable to calculate activation energies for various mechanisms by which dislocations may move in practical cases. During their movements stress fields due to their interactions change and the energy for movement alters. Experimental evidence confirms that the activation energy for thermal recovery of any property affected by dislocations depends on dislocation density and, for a metal such as copper, may typically be found to be of the order of 1–2 ev at around 200°c (Phillips and Phillips 1952).

2.3. *The Significance of 'Increase in Resistivity'*

Two methods of presenting measurements of the change in resistivity have been used. The first, that of giving simply the absolute change in resistivity, $\Delta\rho$, is particularly appropriate where the behaviour of any one metal is being studied. Since Matthiessen's Rule is generally well obeyed by deformed metals (§ 5.5), $\Delta\rho$ is independent of temperature of measurement (always provided this is not so high that recovery occurs). The second method, that of giving the increase in resistivity relative to the resistivity of defect-free metal, $\Delta\rho/\rho$ (usually expressed as a percentage) is often more convenient from the experimental point of view, but as the resistivity of the annealed metal varies with temperature it is always necessary to give a value for the reference resistivity or at least to specify the temperature of measurement.

It is frequently tacitly assumed that the relative increase in resistivity, $\Delta\rho/\rho$, is a valuable basis for comparing the behaviour of dissimilar metals treated in the same manner at the same temperature. One reason for this is the intuitive feeling that the resistivity of a lattice defect should be related to the resistivity of the defect-free lattice. Further support comes from an analogy between melting and the introduction of defects suggested by Nicholas (1953, private communication). It is well known that for pure metals with a f.c.c. structure, the resistivity is approximately doubled by melting and Nicholas has pointed out that this is also true for a number of alloys (with the same structure) where the absolute resistivity change varies over a wide range. On the other hand, calculations of the effect of defects on electrical resistivity (§ 2.1) generally derive an expression which gives $\Delta\rho$ in terms which do not explicitly include the resistivity of defect-free metal. In view of these considerations and the complications which arise owing to the differing mobilities of defects in different metals at the same temperature, it is clear that considerable caution must be exercised in comparing a resistivity change in one metal with that in another.

§3. Quenching Experiments

The thermodynamic equilibrium of a given type of defect in a metallic lattice is dependent on two quantities. These are the free energy of formation of each defect and the contribution made by the defects to the entropy of the system. The energy of formation causes an increase in the total free energy of the system but the presence of defects increases the entropy to a degree calculable from their nature and concentration, so causing a decrease in the free energy. It can readily be shown that at any temperature there is a concentration of defects for which the energy of the system is a minimum. The equilibrium concentration of defects decreases with decreasing temperature and is zero at absolute zero but of course in practice it is impossible to maintain equilibrium on cooling simply because defects cannot diffuse readily at low temperatures and are prevented from migrating out of the lattice. They then become ' frozen-in '. This happens on slow cooling but it is obviously possible to cool rapidly or quench from a high temperature and so attempt to freeze-in the concentration of defects appropriate to the high temperature. Although these considerations have long been understood it is only recently that experimental attempts have been made to use quenching experiments as a source of defects and as a means of obtaining heats of formation.

As will be shown below, the importance of quenching experiments lies in the fact that the only types of defect likely to be quenched-in in appreciable concentration are vacancies and vacancy pairs. Such experiments offer the possibility of studying their behaviour without the complications that arise when appreciable concentrations of other defects such as interstitials and dislocations are present.

3.1. *Theory*

3.1.1. *The Equilibrium Concentration of Defects*

It is a familiar result of statistical thermodynamics that the equilibrium concentration, c, of any species of defect is given by

$$c = \exp\{-(\Delta H_f - T\Delta S)/kT\}$$

where ΔH_f is the enthalpy (heat) of formation of the defect and ΔS_f is the change in entropy (other than the entropy of mixing) associated with each defect. Theoretical estimates of ΔH_f are available for various defects in copper so that with the assumption that $\Delta S_f/k$ is of order unity we can give estimates of defect concentration at various temperatures :

	ΔH_f (ev)	Defect concentration		
		0°c	500°c	1000°c
Vacancy	~ 1 Huntington & Seitz 1942	10^{-18}	$10^{-6\cdot5}$	$10^{-3\cdot9}$
Interstitial	~10 Huntington 1942	10^{-180}	10^{-65}	10^{-39}
Vacancy pair	~1·6 Bartlett & Dienes 1953	10^{-29}	10^{-10}	$10^{-6\cdot3}$

From these estimates and the calculations summarized in § 2.1 it is clear that measurable effects in quenching experiments will only be produced by vacancies. Here it may be noted that dislocations cannot be treated in the same manner as vacancies and interstitials, because the presence of dislocations in a lattice will not cause a lowering of the free energy (Seitz 1952 b).

By making the assumptions that in an ideal quenching experiment (all defects retained), the ' quenched-in resistivity ', $\Delta\rho_Q$, is proportional to the concentration of quenched-in defects, and that the defects are only of one type, it becomes possible to determine ΔH_f from measurements of the variation of $\Delta\rho_Q$ with quenching temperature T_Q.

We have

$$\ln \Delta\rho_Q = -\Delta H_f/kT + \Delta S_f/k + \ln A$$

where $A = \Delta\rho_Q/c$. Further, for vacancies in pure f.c.c. metals an estimate of ΔS_f can be found from diffusion theory if the activation energies for self-diffusion and for movement of vacancies are known (Zener 1952). Thus in principle it is also possible to determine A, the increase in resistivity for ' unit concentration ' of vacancies.

3.1.2. *Conditions for Quenching-in Defects*

In an ideal quenching experiment the high-temperature concentration of defects is preserved unchanged at the lower temperature at which the defects are frozen-in. With a finite cooling rate this cannot be achieved because of various processes which tend to maintain thermodynamic equilibrium by eliminating excess defects.

Nabarro (1948) has pointed out that dislocations can act as sinks for vacancies and Seitz (1950 b) has estimated for copper that on this basis something approaching the concentration of vacancies at 1000°c might be preserved, if quenching to the freezing-in temperature were carried out in less than 0·1 sec. Bartlett and Dienes (1953) have indicated that, in non-equilibrium conditions such as encountered in quenching, some vacancies will combine to produce vacancy pairs (§ 2.2.1). Other possible mechanisms can be envisaged for the removal of excess vacancies either by annihilation at sinks or by the formation of secondary defects. Rigorous theoretical treatment of all the possibilities is impossible, so that experimental tests are necessary to show what concentrations of particular defects are quenched-in under varying quenching conditions. It should then be possible to extrapolate observations to find the effect of an infinitely rapid quench.

3.2. *Experimental Results*

In addition to the complications discussed in § 3.1.2 there are two other factors to be kept in mind. The first is purity of material. Quenching effects have been reported which were almost certainly caused by the solution of an impurity at a high temperature (e.g. Blazey 1936). The solubility of many impurities will vary with temperature in a manner

similar to the concentration of defects and so give rise to a spurious 'heat of formation'. The second factor is that quenching may cause plastic deformation by reason of the stresses set up as outer and inner regions of a specimen are cooled at different rates. This deformation will create lattice defects whose effects may be confused with those of quenched-in defects.

Although quenching experiments offer a unique opportunity for determining the properties of vacancies, *per se*, only a few preliminary experiments have yet been carried out.

3.2.1. *Pure Metals*

The only satisfactory measurements that appear to have been made are those of Kauffman and Koehler (1952). Gold wires of 99·999% purity were heated at various temperatures before being rapidly cooled to room temperature in 7 ± 3 milliseconds by means of a blast of gaseous helium. The wires were then immediately immersed in liquid nitrogen and resistance measurements made. Typical increases in resistance were 0·065% produced by quenching from 690°C and 0·82% produced by quenching from 920°C. The large increase in the quenched-in resistance produced by increase of quenching temperature was taken to indicate that quenching strains were not the source of the resistance changes. The authors stated there was some difficulty in measuring the precise quenching temperature and they were only able to give a preliminary estimate of ΔH_f as lying between 1 and 2 ev. Recovery experiments showed that about a third of the quenched-in resistance annealed out at around room temperature, and that the remainder annealed out between 100° and 500°C. The activation energy for the first process was found to be $0{\cdot}4\pm0{\cdot}14$ ev. This is surprisingly low for the movement of single vacancies according to theory and experiment (cf. § 6.1), but as Bartlett and Dienes have shown it is likely that appreciable concentrations of pairs were frozen-in. It therefore seems probable that the observed 'activation energy' was not unique and that recovery due to the movement of single and paired vacancies was occurring concurrently. The retention, in Kauffman and Koehler's experiments, of two-thirds of the quenched-in resistance after the 0·4 ev recovery stage is a notable but fairly common observation (cf. § 4.2). It suggests that defects were not being completely removed but rather were interacting with each other or with other structural imperfections to give secondary defects with higher activation energies for movement.

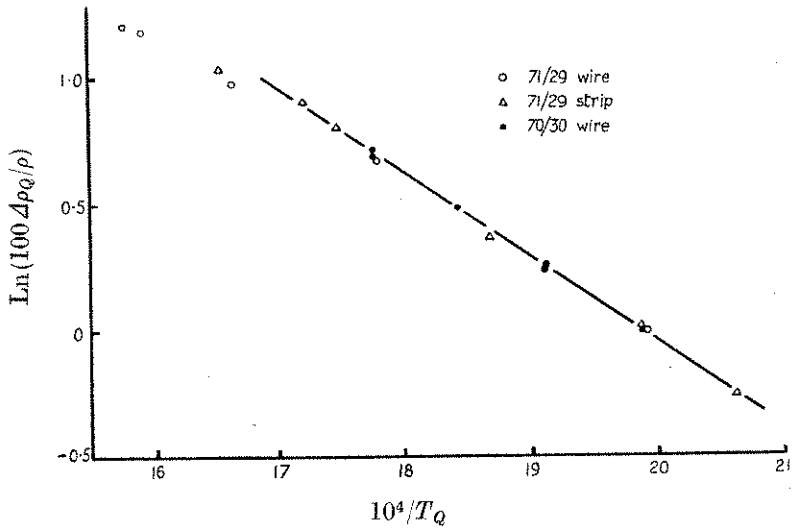
3.2.2. *Alloys*

An additional complication in alloys is that temperature-dependent rearrangements of the constituent atoms may occur giving rise to long- or short-range order or to clustering.

As an example of an alloy which is not known to possess an ordered structure we may consider α-brass. It has been found (Broom, Stacey and Westwood 1953) that the resistivity of annealed 70/30 and 71/29

brass measured at −183°C is sensitive to rate of cooling even from temperatures as low as 200°C. The lowest resistivity was obtained by slowly cooling a specimen from 500°C to room temperature before placing it in liquid air. Quenching experiments were then performed by heating the specimen in a salt bath for a few minutes and then rapidly plunging it first in iced brine and then in liquid air. The relationship between quenching temperature, T_Q, and the relative increase in resistivity, $\Delta\rho_Q/\rho$, is shown in fig. 1. Excellent agreement was obtained with wires of differing dimensions so that it is unlikely that the effect was due to quenching strains ; the agreement also suggests that the high-temperature concentration of defects was effectively maintained. Further, the

Fig. 1



Change in resistivity, $\Delta\rho_Q/\rho$, produced by quenching annealed α brass from temperature T_Q(°K). (Measurements at −183°C, $\rho_{-183}\simeq 4\,\mu\Omega$cm.)

changes occurred so rapidly, even at relatively low temperatures, that it is unlikely that they were due to the solution or precipitation of impurities. The slope of the curve in fig. 1 gives a value of $\Delta H_f=0{\cdot}34$ ev for the type of defect responsible for the quenched-in resistance.

Although this appears rather low, it is not impossible that it represents the energy of formation of vacancies in the alloy. Nowick and his co-workers (see Roswell and Nowick 1953) by measurements of stress-relaxation and internal friction have found a value of $\Delta H_f=0{\cdot}5$ ev in a 70/30 silver–zinc alloy quenched from similar temperatures. Low values of ΔH_f for vacancies in the alloys may be attributed to the ease of their formation in the middle of clusters of zinc atoms (LeClaire 1953, private communication).

In fig. 1 the deviation from linearity above about 310°C may be due to the difficulty, with the technique used, of quenching-in vacancies above this temperature.

Annealing experiments in the range 50°–100°C showed that recovery of part of the quenched-in resistance took place with an activation energy of $1{\cdot}0 \pm 0{\cdot}2$ ev. Again, this gives indirect support to the vacancy hypothesis as from evidence given by the Kirkendall effect, Seitz (1950 b) has concluded that vacancies in brass move preferentially via zinc atoms. We should then expect the sum of the two measured activation energies ($1{\cdot}4 \pm 0{\cdot}2$ ev) to approximate to the activation energy for diffusion of zinc atoms, which has been found by Correa da Silva and Mehl (1951) to be 1·35 ev for the composition used.

There is, however, an alternative explanation of the observations. This is simply that there exists short-range order in α-brass which affects the resistivity, even though it is not certain that short-range order can have an appreciable effect on resistivity (§ 6.3). However we should expect that the activation energies for the ' destruction ' and ' establishment ' of short-range order would be equal. Further, in quenching experiments on a 70/30 silver–zinc alloy Nowick has deduced that there was no change of short-range order, and this would of course be more likely in the silver–zinc alloy than in the brass because of the larger difference of atomic radii. The observations of Masumoto, Saito, and Sugihara (1952) on a specific heat anomaly in α-brass and attributed by them to short-range order are of interest, but it is noteworthy that they find a maximum effect at a lower temperature, *c.* 230°C, than that found in the resistance experiments.

Important experiments on quenched-in defects in silver–zinc alloys have been carried out by Nowick using stress-relaxation and internal friction measurements to detect defects and recovery stages (see Roswell and Nowick 1953). The original papers should be consulted for details of this work.

3.2.3. *Ordered Alloys*

Much smaller concentrations of vacancies can be detected in ordered alloys than in pure metals because in partially ordered alloys they are capable of promoting ordering which results in large resistivity changes. Dugdale and Green have determined activation energies for ordering after quenching Cu_3Au from just below the critical temperature. Their results are best considered in § 4.2.3 in conjunction with other work on the same specimens.

Brinkman, Dixon and Meechan (1953) have studied the effect of quenching temperature on the initial rate of ordering of disordered Cu_3Au. The rate increased with increasing quenching temperature in the range 542°–704°C in conformity with the supposition that more vacancies were being quenched-in on cooling from high temperatures than from low. Ordering was observed at 150°C and because of the effect of

quenching temperature this was confidently ascribed to the movement of vacancies.

§ 4. Irradiation Experiments

It is clear that if a high energy particle enters a metallic lattice and collides with an atom, there will be generated some form of transient or permanent lattice defect. Although this has long been realized it is only in recent years that large fluxes of high-energy particles have become available through the development of accelerators and neutron reactors, and that any study of interactions has been made. By far the most useful technique in the experimental investigation of irradiation phenomena has been the measurement of electrical resistance and in turn such measurements have revealed important similarities in the properties of lattice defects formed by irradiation and by other methods such as quenching and deformation. Useful reviews of irradiation effects in solids have been given by Slater (1951), Siegel (1953) and Dienes (1953).

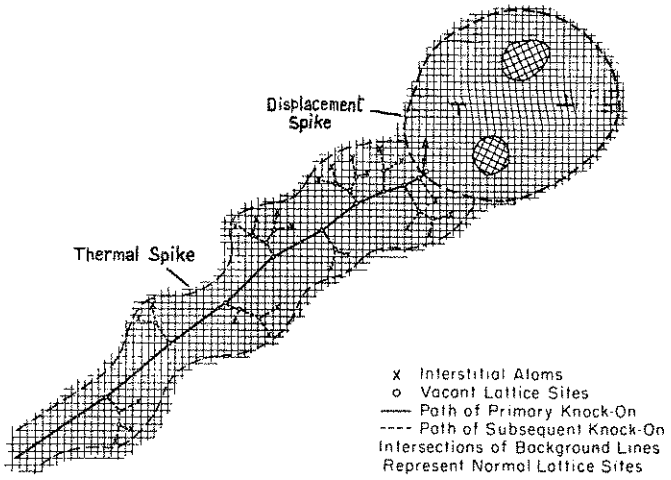
4.1. *Theory*

Formal treatments of the interactions between high energy particles and metallic lattices have been given by Seitz (1949) and by Brinkman (1953) and will not be reproduced here. The particle may in general lose kinetic energy by exciting electrons attached to the atoms of the lattice and by elastic collisions with stationary nuclei. The first process is important at high energies and virtually results in the formation of a filament of heated material in the wake of the particle. This has been termed a ' thermal spike ', and experimental effects have been observed which are explicable in terms of very rapid heating and quenching of small volumes. On the other hand, elastic collisions may result in the displacement of atoms from normal lattice sites to give vacancies and interstitials and some of these knocked-on atoms may then have sufficient energy to cause many more additional displacements in elastic collisions and also give rise to further ' thermal spikes '. Considering the behaviour of an energetic primary knock-on atom, Brinkman (1953) has shown that when its energy falls below a certain value as a result of the processes discussed above, the mean free path between elastic collisions becomes of the order of the inter-atomic spacing and the resulting disturbed region may contain about one to ten thousand atoms. This feature has been given the name ' displacement spike '. The schematic diagram of fig. 2 is taken from a summary by Siegel (1953).

Electron bombardment merits particular attention as it is possible to choose the incident energy so that any collision results in the displacement of a single atom. In order to move an atom from a normal lattice site into an interstitial position it is necessary to give it a definite amount of energy. For example, the displacement energy required for the creation of a vacancy-interstitial pair in copper has been estimated to be 25 ev (Seitz 1949). It is clear that in order to produce defects in any lattice

the energy of bombarding electrons must exceed a threshold value and it can easily be shown that for common metals this value is around 1 Mev which is in the range achieved by conventional accelerators. Increasing the energy of incident electrons above the threshold value will result in increasing separation of vacancy-interstitial pairs formed by collision so that by this means it should be possible to test various hypotheses which interpret recovery results in terms of annihilation of pairs. Although electron bombardments do offer the advantages of greater control and of precision in estimation of the number of displacements

Fig. 2



Bombardment effects in a metallic lattice (schematic: Siegel 1953).

produced, there is the experimental difficulty that relatively few displacements are produced in a convenient bombardment time and so, in pure metals at least, the changes in resistivity are small.

4.2. *Experimental Results*

4.2.1. *Pure Metals*

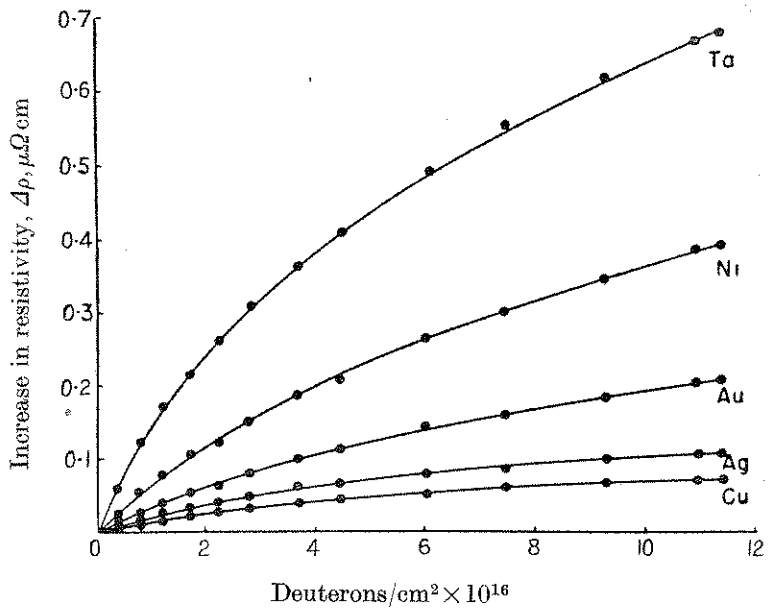
In electron bombardment experiments on pure copper, Eggen and Laubenstein (1953) have found a threshold electron energy above which the change of resistivity during bombardment increased rapidly. This corresponded to a displacement energy of 25 ± 1 ev which is in phenomenally good agreement with the estimate given by Seitz (§ 4.1). Similar measurements on a copper–iron alloy yielded an energy of 26·5 ev for iron atoms (Denney 1952).

Owing to the high mobility of defects produced by irradiation the temperatures of treatment and observation are of great importance and recent experiments have generally been carried out at low temperatures

so that none of the primary defects are lost by combination or annihilation at mosaic boundaries or other internal irregularities. Qualitative results for copper and aluminium bombarded at $-150°$C with α-particles have been given by Martin *et al.* (1951). The resistivity of both metals increased during bombardment, but after annealing at room temperature the aluminium retained no evidence of its irradiation. The only statement about the copper was that it retained an increase of hardness. Recovery was found to have commenced at temperatures as low as $-80°$C.

The most extensive study is that of Marx, Cooper and Henderson (1952). Polycrystalline foils of copper, silver, gold, nickel and tantalum were irradiated with 12 Mev deuterons at temperatures in the region of $-140°$C. Resistivity measurements were made at intervals during irradiation with the results shown in fig. 3.

Fig. 3



Resistivity increases produced by 12 Mev deuterons at about $-140°$C (Marx, Cooper and Henderson 1952).

The increases shown by Cu, Ag and Au are in the order of atomic number as predicted by Seitz (1949). Experiments at an average temperature 10°C lower gave higher increases in resistivity for a given total deuteron flux and subsequent annealing experiments disclosed the existence of a thermal recovery process operating at a temperature as low as $-165°$C. Pulse annealing experiments were carried out on Cu, Ag and Au between $-100°$ and $-120°$C and assuming a unique rate process for recovery it was found that this recovery occurred with an activation energy of $0{\cdot}2 \pm 0{\cdot}05$ ev. Similar experiments with Ni and Ta

required rather higher temperatures and recovery took place with an activation energy of $0{\cdot}3 \pm 0{\cdot}1$ ev. Annealing experiments at $-165°$C required activation energies of 0·15 ev for Cu, Ag and Au, and 0·2 ev for Ni and Ta to account for the observed recovery.

Finally, annealing experiments at about 28°C were carried out and although these were not of high precision it was deduced that recovery proceeded at this temperature with an activation energy of about 1 ev. Recovery in Cu, Ag and Au at 28°C was nearly complete, but Ni and Ta retained a high proportion of the original increase of resistivity even after an anneal lasting 264 hours.

In discussion of their results Marx *et al.* showed that likely reactions between the vacancies and interstitials produced by irradiation which could give the ' 0·2 ev recovery ' involve the recombination of vacancies and interstitials or the migration of vacancy pairs. There is no reason why recombination of vacancies and interstitials should have a unique activation energy as this will depend on the propinquity of the reactants but the experimental data was not adequate to test whether the observed activation energy was unique. Although vacancy pairs can be assumed to have a high mobility (§ 2.2.1) it would be necessary to assume a high initial concentration of such pairs in order to explain the results. In view of the ' high ' activation energy for movement of primary single vacancies it might be supposed that pairs could only be formed in ' thermal spike ' regions. The recovery observed at room temperature was fairly confidently assigned to the movement of single vacancies in accordance with calculations summarized in § 2.2.1.

The work of Marx *et al.* has been followed by more detailed investigations of annealing in copper of 99·99% purity irradiated by 12 Mev deuterons. Overhauser (1953) found that most, if not all, of the initial bending in low temperature resistivity-bombardment curves (cf. fig. 3) was due to annealing at the bombardment temperature. Between $-185°$ and $-180°$C the estimated activation energy for recovery was 0·2 ev. In recovery experiments between $-180°$ and $-60°$C various activation energies were reported ranging from 0·2 ev to about 0·6 ev : this behaviour was attributed to the ease of annihilation of very close vacancy-interstitial pairs due to the local strains developed. These strains would vary depending on the particular configuration created, and so account for the spread in activation energies.

At around $-30°$C recovery was characterized by a unique activation energy of $0{\cdot}68 \pm 0{\cdot}02$ ev and its rate could be accounted for by means of a modified second-order reaction equation. This indicated that recovery proceeded at this temperature by the volume diffusion of *vacancies* to interstitial atoms with resulting annihilation. Calculations showed that the presence of interstitial atoms was sufficient to affect the migration of vacancies by reason of the elastic strains introduced and that this accounted for the deviation from second-order kinetics (for high concentrations). A discussion of vacancy-interstitial annihilation kinetics has also been given by Brown, Fletcher and Machlup (1953).

About one half of the original increase in resistivity disappeared on annealing below −60°C and a further quarter at around −30°C. The remaining quarter was not removed below 170°C and may have been due to the disordered regions associated with thermal and displacement spikes. Such disorder could probably only be removed by a treatment corresponding to recrystallization.

Further experiments on copper of 99·9% purity have been reported by Eggleston (1953). Bombardments by 35 MeV alpha-particles were carried out below −150°C. Recovery experiments in the range −65° to 20°C revealed an apparently unique activation energy of $0{\cdot}72 \pm 0{\cdot}02$ ev. This is in good agreement with Overhauser's value of $0{\cdot}68 \pm 0{\cdot}02$ ev and with a value of $0{\cdot}67 \pm 0{\cdot}09$ ev for cold-worked copper (Eggleston 1952). After annealing at room-temperature only about one quarter of the irradiation-induced resistance remained and further isothermal anneals between 250° and 300°C gave results which were interpreted as indicating an activation energy of about 2·1 ev in this range. This result is comparable with the 2·2 ev recovery found by Redman, Coltman and Blewitt (1953) in measuring the critical shear stress of pile-neutron irradiated Cu single crystals after anneals between 305° and 385°C. Some comparisons were made with the recovery of resistivity of a copper wire twisted in liquid helium. Up to −80°C the rate of recovery was about the same but between this temperature and 20°C the resistivity of an irradiated sample recovered much more rapidly. Above 100°C the position was reversed and at higher temperatures part of the radiation damage tended to persist (see also Siegel 1953). This is in contrast with an observation of Dugdale (private communication) that in platinum almost all the increase in resistivity caused by pile-neutron bombardment could be removed by heating at about 200°C.

Table 1. Recovery of Resistance in Platinum

Specimen	Initial increase in resistivity (at 0°C) (%)	Decrease in extra resistance* (%)	Activation energy (ev)
Irradiated	0·2	13	1·19
Irradiated	0·2	17	1·19
Cold-worked	1·5	13	1·20

* Decrease during 640 hr. at 70°C followed by 336 hr. at 90°C.

Dugdale (1952) has subjected platinum to neutron bombardment at 50°C and determined activation energies for recovery at a mean temperature of 80°C. His results, summarized in table 1, have great interest as they indicate that the same defect is responsible for part of the increase in resistivity both in deformed and irradiated specimens. Mott (1952) has specifically identified these defects as vacancies.

4.2.2. *Alloys*

Rather curiously, no extensive measurements have been made on the effect of irradiation on the resistivity of alloys other than those showing order–disorder phenomena.

Billington and Siegel (1950) have reported increases in resistivity in a solution-treated 2% beryllium–copper alloy when subjected to neutron bombardment. In contrast to observations on disordered Cu_3Au (discussed below) the relative increases were fairly large (~15%) and persisted at room temperature. It is possible that they were due to trapping of defects by solute atoms; this view accords with the observation that smaller increases were obtained in aged alloys. In a two-phase alloy there would be fewer beryllium atoms in solution, and also there would be a large number of internal surfaces where defects could be annihilated. Later work on the same alloy reported by Siegel (1953) and Dienes (1953) indicates the effectiveness of neutron bombardment in assisting the formation of beryllium-rich nuclei.

4.2.3. *Ordered Alloys*

The earliest reported experiments are those of Siegel (1949) who exposed samples of ordered and of disordered Cu_3Au to a fast neutron flux in a nuclear reactor. The temperature during bombardment was near 40°C and all resistance measurements were made at 25°C. The results obtained are shown in table 2 where the first column gives the integrated neutron flux for neutrons with an energy higher than 50 kev.

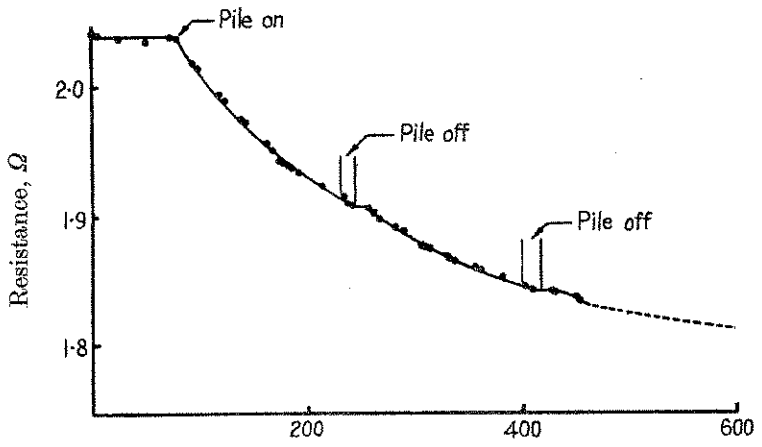
Table 2. Neutron Bombardment of Cu_3Au

Neutron flux (neutrons/sq. cm)	Resistivity before and after irradiation	
	Initially ordered specimens ($\mu\Omega$cm)	Initially disordered specimens ($\mu\Omega$cm)
0	4·60	11·20
$0{\cdot}4\times10^{19}$	5·71	11·25
$0{\cdot}6\times10^{19}$	6·25	11·25
$1{\cdot}0\times10^{19}$	7·54	11·17
$1{\cdot}5\times10^{19}$	8·36	11·21
$3{\cdot}3\times10^{19}$	10·10	11·30

X-ray diffraction experiments confirmed that the initially ordered specimens had become disordered during irradiation. The small increases in resistivity in the originally disordered specimens could be accounted for by the formation, through neutron capture by gold, of ^{198}Hg. Using the calculation of Seitz (1949), Siegel deduced that only a few per cent of the atoms in the originally ordered alloy could have been displaced from their positions by direct collision, and so the observed disordering must be accounted for in terms of the very rapid quenching in regions of high temperature spikes produced in the tracks of recoil atoms.

A study of the effect of neutron bombardment at 200°C on the resistivity of disordered Cu_3Au has been made by Blewitt and Coltman (1952). These workers did not specify the original disordering treatment used, nor the original resistivity, but assumed from data of Sykes and Evans (1936) that their specimen had a relaxation time of 10^5 hours at 200°C. Their results are shown in fig. 4. During the course of the experiment the pile was shut down on two occasions, and during these periods, the resistance continued to fall. The interpretation of these results is that irradiation produced lattice defects (vacancies and interstitials) which, at the temperature employed, allowed ordering to proceed. From the estimated time taken to reach equilibrium and from the number of displaced atoms, Blewitt and Coltman deduced that each displaced atom affected, on average, a region about 60 Å in diameter.

Fig. 4



Ordering of Cu_3Au at 200°C, under fast neutron flux of 10^{12}n/cm²/sec (Blewitt and Coltman 1952).

This was in agreement with an estimate of domain size and was taken to indicate appreciable mean free paths of the defects before annihilation. Later work by Halteman, Mecklin and Glick (1952) has shown that ordering can proceed at 200°C at rates comparable with those observed by Blewitt and Coltman simply during isothermal anneals and without irradiation. Two prior disordering treatments were given and in both of these it is likely that defects were quenched-in. Presumably it was these defects which fulfilled the role played by irradiation-induced defects in the Blewitt and Coltman experiments, but it is somewhat surprising that their efficacy was persistent for periods of up to 150 hours.

Coltman and Blewitt (1953) have recently given further evidence for the ordering at 150°C of neutron-irradiated specimens which " had a

degree of order corresponding to equilibrium at 370°C ". One bombardment was carried out at −160°C and a small increase in resistivity was observed. Annealing at −80°C following irradiation produced no change in resistivity but a small decrease was caused by heating in the range 0° to 150°C. No appreciable changes resulted from heating non-irradiated specimens at 150°C.

Glick, Brooks, Witzig and Johnson (1952) and Glick and Witzig (1953) have studied the effect of neutron irradiation at 80° and 140°C on Cu_3Au. Initially ordered samples first showed a fall in resistivity, presumably due to the creation of a few defects which allowed further ordering to proceed. At higher total neutron fluxes the resistivity increased above the original values, the increase being more pronounced in the case of the 80°C irradiation. X-ray examination of filings similarly exposed showed only small decreases in the long-range order parameter, but an increase in lattice spacing (Fillnow, Halteman and Mechlin 1953). These results are similar to some found by Adam and Dugdale (1951) for an ordered alloy 'Cu_7 Au_3'; resistance changes were measured and it was noted that X-ray diffraction superlattice lines remained sharp. Glick *et al.* further showed that an initially disordered specimen of Cu_3Au irradiated at 80°C gave an initial fall in resistivity followed by a slight rise towards the original value, which was not exceeded. At 140°C only a decrease was observed.

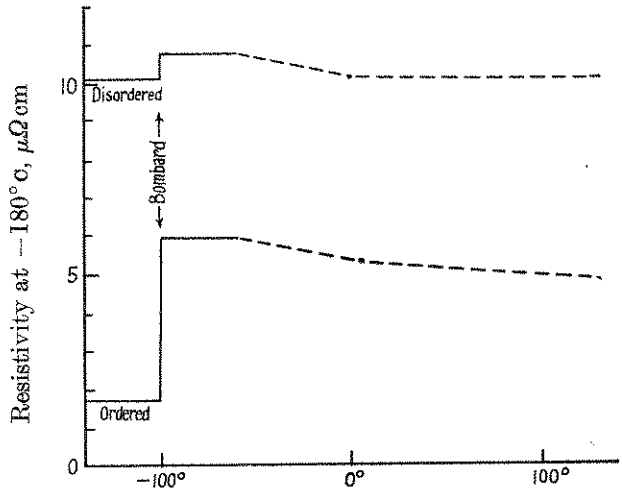
Similar experiments in this field have been reported by Martin *et al.* (1951) who subjected specimens of Cu_3Au and CuAu to bombardment with α-particles at −150°C. Large changes in resistivity were observed at the temperature of bombardment; subsequent annealing experiments showed that recovery began at temperatures as low as −80°C. After an unspecified time at room temperature it was found that originally ordered specimens of Cu_3Au and of CuAu retained large changes in resistivity, temperature coefficient of resistivity and lattice parameter and these were such as to indicate that the alloys had been disordered by bombardment. Only small changes in these properties were retained by originally disordered specimens.

Experiments by Dixon, reported by Siegel (1953), on the irradiation of ordered Cu_3Au by α-particles at −180°C and +220°C showed that disordering occurred during the course of both irradiations, but that it was much slower at 220°C by reason of the fact that vacancies created by irradiation were able to diffuse and 'put right' the disorder caused by thermal and displacement spikes. Evidence for the strictly local generation of disordered regions by irradiation has been obtained by Stello (see Siegel 1953, Dienes 1953) in the course of studies on the annealing kinetics of CuAu and Cu_3Au disordered by thermal treatment. by cold-work and by irradiation.

The effects of the primary defects, vacancies and interstitials, produced by proton bombardment of Cu_3Au have been carefully studied by Brinkman, Dixon and Meechan (1953). Specimens of ordered and of

disordered Cu_3Au were given equal irradiations with 9 MeV protons at a temperature below $-100°C$ and then pulse annealing experiments were carried out at temperatures up to 130°C. The results are shown diagrammatically in fig. 5. It had been shown (§ 3.2.3) that annealing at around 130°C was to be attributed to vacancy migration causing ordering so that it was concluded that the recovery observed both in ordered and disordered Cu_3Au at around $-30°C$ was due to the movement of *interstitials*. Following Overhauser (§ 4.2.1) it was assumed that these interstitials were annihilated mainly by combination with vacancies but also by dislocations and mosaic or grain boundaries. After the $-30°C$ recovery there would therefore be left some vacancies to promote order when they could move freely at 130°C. The small effect in disordered Cu_3Au was attributed to the difficulty of creating order without the prior

Fig. 5



Resistivity changes in Cu_3Au caused by proton bombardment below $-100°C$ followed by pulse annealing up to 130°C (schematic: data from Brinkman, Dixon and Meechan 1953).

existence of long-range order domains. Subsidiary calculations were made to show that interstitialcy diffusion would be unlikely to cause ordering in Cu_3Au. As the $-30°C$ recovery was not fully investigated it is just possible that it may correspond to the annihilation of close vacancy-interstitial pairs found by Overhauser to occur in bombarded copper between $-180°C$ and $-60°C$ with activation energies between 0·2 and 0·6 ev. Other aspects of the work of Brinkman *et al.* will be discussed in §§ 5.4.3 and 6.1.

In contrast to the behaviour of Cu_3Au when bombarded by massive particles, irradiation by 1 MeV electrons at low temperatures results in

no significant change in the resistivity of an ordered alloy (Dixon, Meechan and Brinkman 1953). A treatment which should have resulted in an increase of 5% gave less than 1% and it was concluded that the separation of the vacancy and interstitial produced by any one collision must have been so small that recombination was rapid even at −195°C. However some decrease in resistivity (further ordering) was observed on annealing at room temperature and it is likely that this was due to the movement of the few 'stable' vacancies produced during irradiation at the low temperature. Some irregularities in the annealing data were found and no suggestion was made to account for these. Adam, Green and Dugdale (1952) had previously shown that bombardment with 1- and 3-Mev electrons at about 40°C produced no measurable change in resistance in a well-ordered specimen of Cu_3Au, but that on subsequent annealing at 100°C further ordering occurred. Heating at 100°C before bombardment produced no increase in order.

Further studies by Dugdale and Green (private communication; see also Broom 1953) have concentrated on determining activation energies for ordering using the method previously described by Dugdale (1952). Small specimens of Cu_3Au were heated at 380°C to form large domains and then quenched in water. The activation energy for ordering within the domains was measured between 70° and 130°C and found to be $0{\cdot}88\pm0{\cdot}14$ ev. One specimen was then bombarded at room temperature with 1 Mev electrons and the rate of ordering was observed to increase: the activation energy was remeasured in the range 0° to 100°C and found to be $0{\cdot}84\pm0{\cdot}08$ ev. Another specimen was lightly deformed after quenching: the activation energy in this case was $0{\cdot}97\pm0{\cdot}12$ ev. The approximate correspondence between all these values can be regarded as indicating that the same mobile defects, presumably vacancies, were responsible for ordering in the several cases. Some studies of ordering kinetics in CuAu have been made by Stello and reported by Dienes (1953). These appear to be more complex.

Radiation damage in β brass has been observed by Eggleston and Bowman (1953). In their experiment, foils of β brass were bombarded with 33 Mev α-particles at temperatures lower than −100°C. Resistance changes were considerably higher than would have been observed in corresponding experiments on copper so that it is very probable that disordering was the cause of the large effect. In addition, pulse annealing experiments showed that as little as 5 min at 0°C was sufficient to eliminate all the bombardment-induced resistance. This is in accordance with the well-known rapid ordering of β brass.

The effect of irradiation on order–disorder alloys is clearly dependent on the temperature of bombardment. At low temperatures where atomic mobility is low, frozen-in defects will be produced which in an initially ordered alloy can only have the effect of producing disorder. At high temperatures any alloy will be assisted towards order by irradiation-produced defects which allow atom migration to occur. These are the

major factors in electron bombardment when the formation of thermal and displacement spikes is small, but when bombardment is by heavy particles and when recoil atoms have high energy, the creation of such regions is the major cause of disordering.

§ 5. Deformation Experiments

The simplest and most widely practised method for the introduction of defects into metallic lattices is that of deformation. There is therefore a much greater body of diverse experimental data to be surveyed in this section than in §§ 3 and 4. Some 150 publications on this topic have appeared since the pioneer work of Becquerel (1846) but much of the data is of little present value owing to the neglect of experimental precautions now recognized as essential. Where a choice between differing results has been necessary, preference has been given to results judged to refer to the purest metal or the simplest alloy.

5.1. *Theory*

In view of the many excellent reviews of the general properties and mechanism of production of lattice defects formed during slip (for example, Mott 1952, 1953, Seitz 1952 a, Cottrell 1953 a, b) it is only necessary to give here a brief summary of the principal relevant features.

5.1.1. *Vacancies and Interstitials*

These may be created, according to Seitz (1952 a) in several ways. First, by a purely geometrical means when screw dislocations moving in different planes intersect. It is difficult to estimate how many defects arise in this way during plastic deformation as there is great variety in the possible arrangements of dislocations within a plastically deformed metal. Second, intense local heating in the lattice, due to the shortening of a dislocation line in a high stress field or to the annihilation of pairs of dislocations of opposite sign, can cause dispersion of defects produced geometrically and also, independently of this, may cause the evaporation of defects from the dislocation. It is considered unlikely that the creation of stable vacancy-interstitial pairs could readily occur as the energy for their formation is probably high, $\sim$10 ev (Huntington 1942), and they would be able to recombine very easily except at the lowest temperatures. A third mechanism of creation is during movement of a dislocation which has a jog. There will be a tendency for atoms to be added on to, or lost from, the extra half-plane at such sites and because greater energy is required to create interstitials than vacancies, a preponderance of vacancies will be formed by this process. It should be noted that these methods of generation do not necessarily lead to the effective dispersal of single vacancies or interstitials. For instance, geometrical considerations may require the formation of a planar group of vacancies when successive screw dislocations cut a stationary screw dislocation.

5.1.2. *Dislocations*

Current theories of work-hardening generally accept the view that slip takes place by means of dislocations generated at Frank–Read sources, and that hardening occurs due to an increase in the shear stress needed to continue the production of dislocations. For any one source, this may arise due to the ' back pressure ' set up by its own dislocations piled-up against a barrier (Mott 1952, 1953) or it may be caused by fouling produced by lattice defects (Koehler 1952). During work hardening the density of dislocations may rise from about 10^8 to a maximum of 10^{12} lines/cm^2, as shown by measurements of stored energy, x-ray reflections, strain-ageing and magnetic properties (Cottrell 1953 b).

Annealing takes place when the temperature is such that dislocations can climb out of piled-up groups on the slip planes by addition of vacant sites on to the edges of the extra half-planes. This process will lead to softening and in many cases, to polygonization (Cahn 1950). Further softening occurs when the temperature and time are such that dislocations are able to migrate out of the crystal or, by combination of dislocations of opposite sign, annihilate each other.

5.2. *Deformation by Pure Extension*

The literature on the influence of both elastic and plastic extension on the resistivity of metals is extensive perhaps partly because such experiments offer opportunities for measurement of high accuracy in which elegant methods can be employed. An almost complete list of references has been given by Linde, von Heinje and von Sabsay (1950). Despite recent practical interest stemming from the development of resistance strain-gauges it is remarkable how little careful systematic work has been done. It is not intended to review resistivity changes due to elastic strain but it should be stated that they are generally small compared to plastic deformation effects. Generally it is found that resistivity increases or decreases linearly with elastic strain. Results obtained by various investigators show considerable scatter : this is usually attributed to the influence of impurities and preferred orientations in the metals used. Smit (1952) has given a valuable account of the effect of elastic deformation on the resistivity of single crystals.

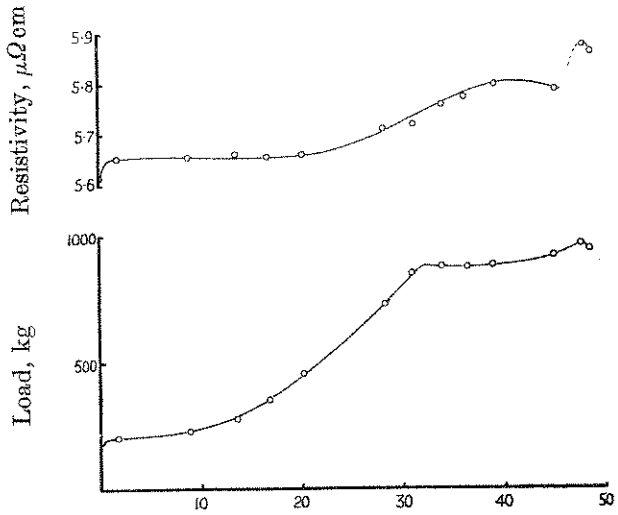
5.2.1. *Single Crystals*

The modes of deformation of single crystals have long been generally understood (Schmid and Boas 1935), but recently observations have accumulated which show that it is possible to extend some crystals of face-centred cubic metals so that they behave like crystals of a hexagonal metal and give linear hardening (Cottrell 1953 a). In pure metals linear hardening is favoured by high purity and by low temperatures. It is also shown by some alloys, notably α brass. Linear hardening ends when slip on a second system begins. None of the resistivity-deformation data discussed below appears to refer to experiments in which linear hardening was observed. It will be obvious that there is a remarkable dearth of

information on resistivity changes during the extension of single crystals. It is hoped that such work will be carried out as it can provide useful information complementary to that yielded, for example, by x-ray and metallographic studies.

5.2.1.1. *Copper.*—Blewitt, Redman and Sherrill (1953 and private communication) have made some resistance measurements on copper single crystals extended at −195°C. Their results will be discussed more fully in § 5.4.1. No recovery of resistivity was observed after shear strains less than 0·25, but no evidence was given to show that the resistivity had changed during the initial deformation. The results are consistent with the view that few lattice defects are created and retained in the lattice during an initial stage of linear hardening. Later work, (Blewitt, private communication) has confirmed that the increase in resistivity for small

Fig. 6



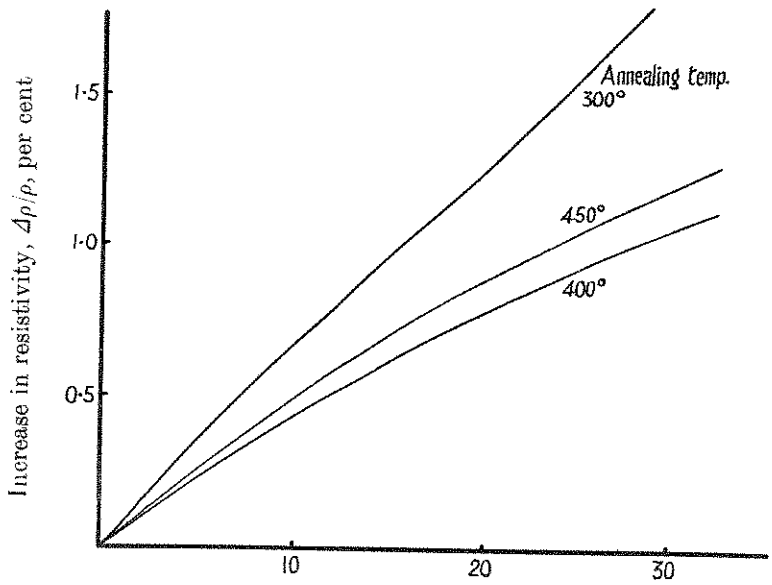
Change in resistivity and yield stress during extension of 72/28 brass single crystal. Double glide began at approximately 25% extension (Masima and Sachs 1928 b).

shear strains is small. Several crystals extended at 4·2°K gave increases in resistivity of about $2\times10^{-3}\,\mu\Omega$cm for a shear strain of 0·25. In contrast to results on α brass (see below) the resistivity rose steadily during the period of linear hardening.

5.2.1.2. *Brass.*—Some experiments of Masima and Sachs (1928 a, b) showed that the resistivity of α brass (72/28) single crystals increased by only about 1% as slip began and then remained constant during almost the whole period when slip was confined to one system, fig. 6. A marked increase was observed as a second slip system became operative ; this can readily be understood, if, for instance, resistivity is appreciably affected by vacancies or interstitials formed by crossing screw dislocations.

5.2.1.3. Cu_3Au.—From experiments on two single crystals Blewitt and Koehler (1950) have deduced three stages during plastic extension and have related them to presumed changes in slip distance and slip band distribution although no direct observations of these features were reported. Up to a shear strain of 0·2 the increase in resistivity was only very slight or, in one case, negative ! This according to the authors may have been due to a reduction in domain wall area. The resistivity then increased fairly rapidly but in the absence of sufficient data it is not possible to know whether this was due to changes in slip-band distribution or to the onset of double slip, as suggested by the experiments of Masima and Sachs, and to be interpreted in terms of defects created by cro.sing screw dislocations.

Fig. 7



Effect of extension at room temperature on the resistivity of pure copper wires annealed in vacuum at the temperatures indicated. (Annealed resistivity presumably about 1·67 $\mu\Omega$cm : Weyerer 1953).

5.2.2. *Polycrystals*

5.2.2.1. *Pure Metals.*—Although it is usually found that the resistivity of an annealed wire increases during plastic deformation there is no general formal relationship between increase in resistivity and extension. Weyerer (1953) has presented data for copper in which resistivity-extension curves (obtained at room temperature) are convex upwards (fig. 7). This is qualitatively similar to data obtained during heavy deformation (cf. fig. 11) and presumably is a result of the impossibility of attaining high concentrations of defects at room temperature owing to their ease of

movement and consequent escape from the lattice. In contrast, some low-temperature experiments give resistivity-extension curves which are concave upwards (fig. 12) and appear to follow a three-halves power law (van Bueren 1953). Here it is likely that very few lattice defects disappear as a result of diffusion and van Bueren has in fact obtained good agreement with experiment by using a dislocation model for the creation of vacancies which are then retained in the lattice.

He supposes that vacancies and interstitials are formed in the wake of jogs which originate when expanding dislocation rings from Frank–Read sources cut other randomly distributed dislocations. For one ring the number of jogs is proportional to its area, which is itself proportional to the strain. The number of vacancies and interstitials is then proportional to the number of jogs multiplied by the average distance each has travelled. Thus the density of vacancies, n_v, (or interstitials) should depend on strain, ϵ, as $n_v \propto \epsilon^{3/2}$. On this model the dislocation resistance should increase approximately proportional to $\epsilon^{1/2}$, so that the increase in resistivity should depend on strain in the following manner:

$$\Delta\rho = A\epsilon^{1/2} + B\epsilon^{3/2}.$$

Results obtained by Manintveld show that copper, silver and gold wires extended between 2 and 11% at liquid air temperature give a relationship of the form

$$\Delta\rho/\rho \propto \epsilon^{3/2}.$$

The proportionality constant is about unity and this is again remarkably consistent with an estimate obtained by van Bueren. It is therefore claimed that for small extensions at low temperatures the contribution of dislocations to resistivity changes is negligible.

These results may be compared with the work of Pry and Hennig (1953) on fine-grained copper wires of 99·999% purity. Wires were extended by regular increments at −195°C, being allowed to anneal at room temperature between increments. Measurements of resistivity were made at each stage and in agreement with previous work (§ 5.4.1) it was found that part of the increase in resistivity annealed out during each period at room temperature. It was then established that at any stage the increase of recoverable resistivity per unit strain depended linearly upon the existing unrecoverable resistivity. If the unrecoverable resistivity is due to dislocations it is clear that the recoverable resistivity per unit strain can reasonably be attributed to defects formed in such a manner that their concentration depends only on the existing number of dislocations. This is consistent with the view that the recoverable resistivity is due to vacancies and/or interstitials generated by the crossing of screw dislocations. However this interpretation takes no account of the *two* sub-zero recovery stages commonly observed (§ 5.4.1). The three-halves power law discussed by van Bueren was not obtained in these experiments and although the vacancy and/or interstitial contribution was relatively large in the early stages of deformation it was not possible to disregard the dislocation contribution.

A further feature of the work of Pry and Hennig was the demonstration that in temperature-cycling experiments resistivity was much more reliable than strain as a guide to yield strength after a change in testing temperature. It is perhaps not surprising that there should be a better correlation between stress and resistivity than between strain and either stress or resistivity simply because both stress and resistivity depend on defect concentration while strain is at least in part a measure of the number of defects that have escaped from the metal.

It is, however, with reference to strain that most resistivity measurements have been carried out. Some typical increases in resistivity for extensions of 10% at room temperature are given in table 3 (*a*).

Table 3. Increase of Resistivity for Extension of 10% at Room Temperature

	Resistivity $\mu\Omega$cm (20°C)	Increase of resistivity %	Reference
(*a*) Cubic metals			
Aluminium	2·65*	0·4	Weyerer 1953
Copper	1·67*	0·55	Aarts and Jarvis 1953
Gold	2·35*	0·75	Aarts and Jarvis 1953
Iron	10·2*	0·3	Weyerer 1953
Silver	1·59*	0·5	Aarts and Jarvis 1953
(*b*) Alloys (composition in at. %)			
70/30 Cu/Zn	6·4*	1·1	Weyerer 1953
50/50 Ag/Au	10·9*	0·75	Aarts and Jarvis 1953
70/30 Co/Ni	10·4	0·75	Broom and Barrett 1953

* From table 4.

An interesting feature of the results of Weyerer (1953) is that for Cu, Al and Fe there was a much higher rate of increase of resistivity for wires incompletely recrystallized than for those completely recrystallized (fig. 7). This gives support to the view that much of the increase in resistivity is due to the formation of vacancies by intersecting dislocations. If it were due mainly to the multiplication of dislocations we might expect a smaller effect in a wire already containing more than the number present in an annealed material. Weyerer also carried out experiments on copper wires of commercial purity annealed under somewhat crude conditions in sealed iron tubes. The results obtained were complex and unpredictable, some even showing a maximum in resistivity–extension curves.

5.2.2.2. *Alloys.*—As with pure metals the increase in resistivity depends approximately linearly on plastic extension. A summary of published data is given in table 3 (*b*).

In contrast to the behaviour of imperfectly recrystallized pure metals (§ 5.2.2.1) Weyerer found no difference between the behaviour of 70/30 brass wires annealed at various temperatures. This suggests that a vacancy mechanism to account for the increase in resistivity is less plausible in the case of α-brass than for pure metals.

Iron–carbon alloys give resistivity-extension curves (Ueda 1930) which are very similar to their stress–strain curves in that they show 'yield points'. According to Cottrell (1948) the yield phenomenon is due to locking of dislocations by carbon atoms from which the dislocations can suddenly break away on application of a sufficiently high stress. Bhatia (1949) has calculated that the resistivity is a minimum in a given alloy when carbon atoms are aligned along the dislocations in atmospheres, so that if this arrangement is disturbed the resulting resistivity-extension curve will not extrapolate to zero increase in resistivity. The return of carbon atoms to dislocations with resulting decrease in resistivity has been studied by Cottrell and Churchman and although discussion of their results is deferred until § 5.4.2 it may be noted that they obtained excellent agreement with the 0·2% sudden increase in resistivity found by Ueda (1930).

5.2.2.3. *Effect of Temperature of Deformation.*—Some results have been reported for Cu, Ag and Au wires extended at 20°, −78° and −183°C (Aarts and Jarvis 1953). Increases in resistivity were always greatest for the lower deformation temperatures and could be well understood in terms of the known ability of certain defects to anneal out of the lattice below room temperature (§ 5.4.1). Similar effects were found in the simple Ag–Au alloy system.

5.3. *Deformation by Wire-drawing and by Rolling*

It is possible to produce a greater deformation in a metal by wire-drawing or by rolling than by simple extension; this of course, leads to a greater concentration of lattice defects and a greater resistance change. The deformation is usually macroscopically much more inhomogeneous; but resistance measurements in such circumstances are analogous to the x-ray examination of filed metals, in that although the precise form of deformation is obscure, the measurements are valuable in indicating the structure of metals in the heavily work-hardened state which is important in manufacturing processes and industrial applications. Some experiments have been made in which deformation was carried out by twisting wires (for example, Calthrop 1926). Although torsion experiments are of attractive experimental simplicity, the deformation is extremely inhomogeneous and the paucity of data does not warrant general discussion in this review.

5.3.1. *Pure Metals*

It is generally found that the resistivity of a pure metal increases rapidly with deformation at first and that the rate of increase then drops off to give a fairly constant resistivity at high strains (e.g. fig. 11).

Therefore, although the only really satisfactory method of showing results is by means of graphs, it is useful to give, in table 4 (*a*), values of the maximum increase in resistivity which it is possible to induce in a metal by reasonably heavy deformation at room temperature. The remarkably high values of increase in resistivity, (relative or absolute), given by molybdenum and tungsten seem to be a result of the very high recrystallization temperatures of these metals so that when deformation is carried out at room temperature a very high concentration of frozen-in lattice defects can remain in the lattice (see §§ 5.2.2.4, 5.4). That the increases quoted are due to genuine lattice defects and not cracks is shown by the accuracy with which Matthiessen's Rule was obeyed.

In table 4 only data for cubic metals are given, owing to the complication of anisotropy of resistivity in crystals of non-cubic metals.

The form of a resistivity-deformation curve depends, of course, upon the quantity used to characterize the deformation, e.g. the percentage reduction in area or the logarithmic strain. Bearing in mind such differences in presentation of results, there do appear to be some considerable variations in the curves for a given metal as reported by different authors. In particular, although resistivity-deformation curves for copper are usually of the regular form shown in fig. 11, various workers (see e.g. Bardenheuer and Schmidt 1928, Weyerer 1953) have found a pronounced maximum in resistivity-deformation curves. Three factors which may account for the differences will be discussed below; namely, purity of metal and the possibility of precipitation (§ 5.3.3), true temperature of deformation (§ 5.3.5) and finally, the possibility of the formation of internal fissures (§ 5.5). With exact data on the differences in these factors in the various experiments it should be possible to reconcile the various results.

5.3.2. *Single-phase Alloys*

Resistivity-deformation curves of single-phase alloys generally have forms similar to those of pure metals so that again it is valuable to give typical values of the increase in resistivity produced in various alloys by heavy deformation. None of the alloys listed in table 4 (*b*) is known to exhibit long-range order. In selecting data for table 4 (*b*) preference has been given to results for α phase alloys with high solute atom concentrations: for many systems results are available for intermediate compositions. For example, the increase in resistivity given by α phase copper–zinc alloys depends on zinc concentration in the manner shown in fig. 8 (Crampton, Burghoff and Stacy 1941). Similar results were obtained for Cu/Al, Cu/Si and Cu/Sn alloys.

In contrast, it is found that if iron or chromium is added to gold, the increase in resistivity after heavy deformation gradually diminishes with increasing solute concentration, until for alloys containing about 20% of transition metal there is a *decrease* in resistivity on cold-working (§ 5.4.2).

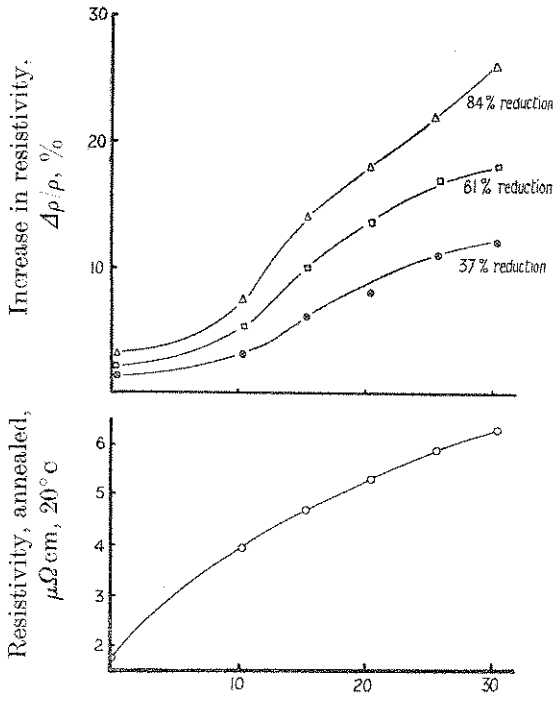
Table 4. Change of Electrical Resistivity with Heavy Deformation at Room Temperature

	Resistivity $\mu\Omega$cm (20°C) (annealed)	Reduction of cross section (%)	Increase of resistivity (%)	Reference
(*a*) Cubic Metals				
Aluminium	2·67	88 (D)‡	0·5	Boas and Nicholas 1953
Copper	1·67	87 (D)	2·4	Smart, Smith and Phillips 1941
Gold	2·35*	98 (R)‡	1·6	Tammann and Dreyer 1933 a
Iron	10·19	85 (D)	1·3	Broom 1952 b
Molybdenum	6·1	>99 (D)	18	Geiss and van Liempt 1927
Nickel	8·21	90 (D)	3·9	Broom 1952 b
Palladium	10·8*	96 (D)	4	Tammann and Dreyer 1933 a
Platinum	10·6*	96 (D)	1	Tammann and Dreyer 1933 a
Silver	1·59*	98 (D)	5	Tammann and Dreyer 1933 a
Tungsten	5·49	>99 (D)	50	Geiss and van Liempt 1927
(*b*) Alloys (composition in wt. %)				
Copper 7·5 % Al	12·3	75 (D)	33	Crampton, Burghoff and Stacy 1941
10 % Au	~7·8†	97 (R)	1·7	Tammann and Dreyer 1933 b
20 % Mn	~60†	97 (R)	10	Tammann and Dreyer 1933 b
20 % Ni	26·5	84 (D)	3	Crampton, Burghoff and Stacy 1941
3 % Si	22·4	84 (D)	10	Crampton, Burghoff and Stacy 1941
2·4 % Sn	5·4	84 (D)	2	Crampton, Burghoff and Stacy 1941
30 % Zn	6·3	84 (D)	26	Crampton, Burghoff and Stacy 1941
Gold 15 % Ag	~8·2†	97 (R)	1·4	Tammann and Dreyer 1933 b
65 % Ag	10·9	90 (D)	1·1	Broom 1952 b
Platinum 25 % Ir	~33†	50 (D)	0·5	Guillet and Ballay 1923
Silver 25 % Au	~6·4†	97 (R)	0·8	Tammann and Dreyer 1933 b
30 % Cd	—	97 (R)	28	Tammann and Dreyer 1933 b
23 % Zn	—	97 (R)	19	Tammann and Dreyer 1933 b
(*c*) Order–disorder Alloys				
Ag_3Mg ordered	4·8	90 (D)	100	Clareborough and Nicholas 1950
disordered	9·3	90 (D)	8	Clareborough and Nicholas 1950
Cu_3Au ordered	6·5	70 (D)	82	Dahl 1936
disordered	11·6	70 (D)	2	Dahl 1936
Ni_3Fe ordered	—	95 (D)	~35	Dahl 1936
disordered	—	95 (D)	15	Dahl 1936
Ni_3Mn ordered	—	95 (R)	62	Dahl 1936
disordered	—	95 (R)	−3	Dahl 1936
CuZn ordered	5·3	~95 (D)	~40	Honeycombe and Boas 1948

* Metals Handbook (1948) † International Critical Tables (1929) ‡ (D), by wire-drawing; (R), by rolling.

With the exception of Au–Fe and Au–Cr alloys it has always been found that alloying results in a larger absolute increase in resistivity ($\Delta\rho$) for a specified deformation than is given by the pure solvent metal. In some cases there is also a spectacular rise in the relative change in resistivity ($\Delta\rho/\rho$). The caution necessary in attempting to impute significance to apparent differences in 'increase in resistivity' has already been discussed in § 2.3. However it has been suggested that large increases in resistivity (usually taken as relative increases) may be

Fig. 8

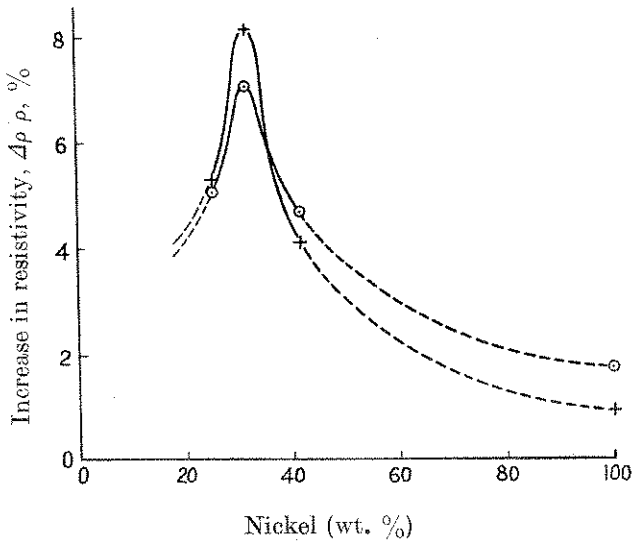


Increases in resistivity produced by deformation of α brasses (Crampton, Burghoff and Stacey 1941).

the result of destruction of undetected long-range order (Crampton, Burghoff and Stacy 1941) or of short-range order which it is frequently assumed affects electrical resistivity in a manner similar to long-range order (Boas and Honeycombe 1948). Nevertheless, there has been found no trace of long-range order in, for example, copper–aluminium alloys where its detection should be simple, nor has there been advanced any direct evidence to support the hypothesis that short-range order has a large effect on resistivity (Nicholas 1953). This latter point will be discussed more fully in § 6.3.

Another explanation has directed attention to possible variations in the form of dislocations in alloys (Broom 1952 b). Heidenreich and Shockley (1948) have shown that a dislocation in a close-packed lattice will dissociate into two partial dislocations separated by a region of faulty stacking, whose size is dependent upon the energy of the wrongly-packed region relative to that of the normally packed lattice. Thus we should expect large stacking faults in face-centred cubic alloys where there is a tendency to transform to a hexagonal phase. For example, in the cobalt–nickel system, a hexagonal phase is stable at room temperature from 0 to 30% Ni and a face-centred cubic phase from 30 to 100% Ni, so that an alloy containing 30% nickel deformed at room temperature might give a large increase in resistivity if this is affected by stacking faults. This hypothesis has been tested (Broom 1952 b,

Fig. 9



The effect of wire-drawing on the resistivity of Co–Ni alloys. 35% reduction of area, + at 100°c, ○ at 0°c. The resistivity of all the annealed alloys was ~10·6 $\mu\Omega$cm.

Broom and Barrett 1953) and found to be satisfactory. Some results obtained by wire-drawing are shown in fig. 9; the large increase at around 30% Ni was confirmed by resistivity-extension measurements and the presence of stacking faults shown by x-ray examination. It should be pointed out that these observations do not prove that stacking faults have a direct effect in scattering the conduction electrons. The presence of large stacking faults during deformation may simply result in a more prolific generation of other lattice defects such as vacancies and interstitials which could be the main agents in increasing the resistivity, although at present no mechanism has been proposed to

show how this can occur. Although discussion has been chiefly concerned with an alloy system where there are adjacent cubic and hexagonal close-packed phases, it is known that in copper–zinc alloys, for instance, an increase in zinc concentration favours formation of large stacking faults (Barrett and Barrett 1951, Warren and Warekois 1953).

Evidence from recovery experiments (§§ 5.4.2, 5.4.3) indicates that in some alloys a high increase in resistivity caused by deformation may arise from the trapping of large numbers of vacancies or interstitials by solute atoms.

5.3.3. *Two-phase Alloys*

A very limited amount of work has been done on alloys consciously recognized as two-phase. In the simplest case, a change in resistivity can result from redistribution of the phases as studied experimentally and theoretically by Chang and Guenot (1950). They showed that deformation of a pearlitic steel results in alignment of the cementite lamellae in the direction of deformation with a resultant *decrease* in resistivity in the longitudinal direction. Some study has been made of resistance changes during deformation of an $\alpha+\beta$ brass (Honeycombe and Boas 1948).

Some unusual results have been reported when deformation is presumably accompanied by precipitation in a supersaturated alloy. Crampton *et al.* (1941) found a 50% increase in resistivity when a solution-treated copper 2·85% cobalt alloy was deformed 84%, but the same alloy when aged before deformation gave an increase of only 5%. Again, deformation of some other age-hardenable alloys sometimes resulted in an initial or even a delayed *decrease* in resistivity. It is not possible to discuss these complex phenomena here but their bearing on the desirability of using pure materials in resistivity studies is obvious. The influence of small concentrations of iron on the resistivity change in copper has been used by Hetherington and Reekie (1951) to estimate the room-temperature solubility of iron in copper.

5.3.4. *Ordered Alloys*

It is apparently possible, by heavy deformation, completely to disorder most alloys which can have an ordered structure in the annealed state. The increases of resistivity are large because the resistivity of the originally ordered alloy rises with increasing deformation to a value generally slightly higher than that of the disordered alloy; see, for example, fig. 10. Some typical results are shown in table 4 (*c*).

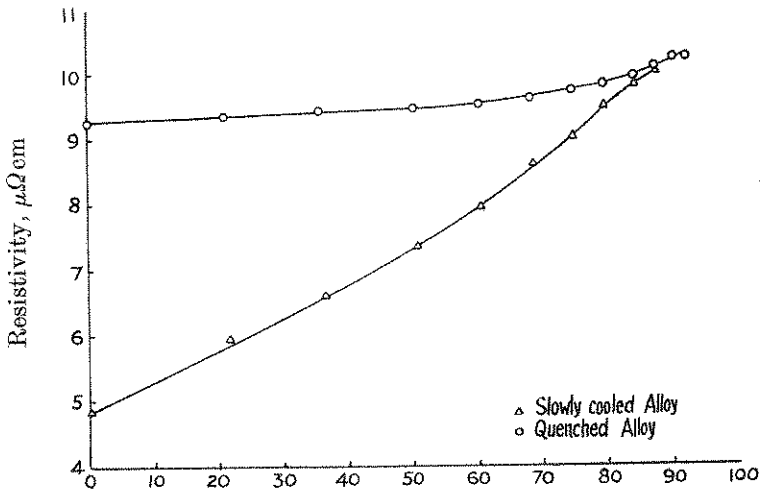
During deformation of ordered alloys, disorder may possibly be created in several ways. First the passage of an odd number of single normal dislocations across a slip plane in an ordered lattice will give rise to an antiphase boundary as each such dislocation is only a partial dislocation in the superlattice. Second, if vacancies are generated during deformation and then move away from the slip plane, a ' filament ' of disorder will result from the motion of each single vacancy in an originally

ordered lattice. However these processes will be difficult and it seems that the most likely cause of disordering is the multiplication of domain boundaries by the passage of dislocations across domains (Cottrell 1953 c).

5.3.5. *The Effect of Temperature of Deformation*

In § 5.3.1 the large increases in resistivity given by molybdenum and tungsten on heavy deformation at room temperature (table 4 (*a*)) were attributed to the fact that these metals are then deformed at a very low temperature relative to their melting points. It has been found (Broom 1952 b) that, if copper and nickel are heavily deformed at low temperature, the increases in resistivity are much greater than are produced by room-temperature deformation, as shown in figs. 11 (*a*), (*b*).

Fig. 10



Reduction in area (per cent)

Effect of cold work on the resistivity of ordered and disordered Ag_3Mg (Clarebrough and Nicholas 1950).

Further, the forms of resistivity-extension curves obtained at −183°C are similar to those for molybdenum and tungsten deformed at or slightly above room temperature. These experiments illustrate the commonsense consideration that the relationship of the temperature of deformation to the melting temperature is of importance in determining the response of a metal to deformation. Results similar to those for copper and nickel were given by iron, 75/25 brass, 50/50 silver-gold and disordered Ag_3Mg. The increase of resistivity due to the disordering of ordered Ag_3Mg was almost independent of deformation temperature in the range 0° to −183°C.

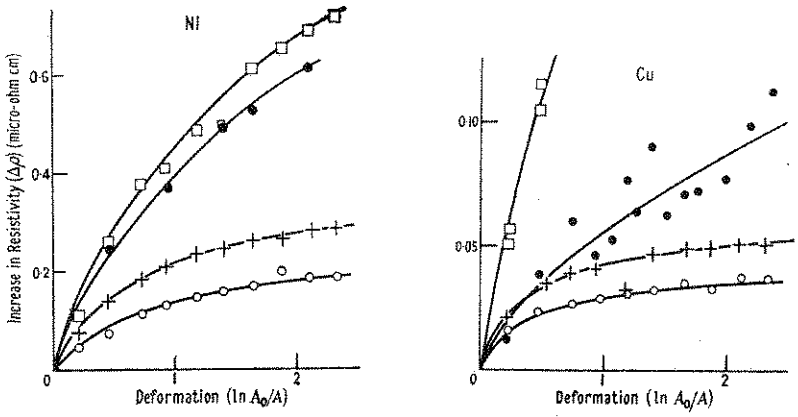
Ellis and Greiner (1952) have measured some resistivities after low-temperature deformation but as their measurements were made at room temperature the separate effects of deformation temperature and subsequent recovery could not be distinguished.

It is possible quite simply to account for the effect of temperature of deformation in terms of lattice defects which are created during deformation and are more readily retained in the lattice at low temperatures than at high (cf. § 5.2.2.4). However, it is interesting to note that Mott (1952), in specifically considering vacancies, has given diagrammatic stress–strain curves for various temperatures which are very similar to the resistivity-strain curves found for nickel (fig. 11 (*a*)).

5.4. *Recovery of Resistivity*

It appears to be a general observation that the resistivity of a deformed metal can change isothermally at temperatures which may be only slightly higher than the temperature at which deformation was carried out. Most frequently the resistivity decreases towards the value for the annealed material, and the term ' recovery of resistivity ' is most appropriate.

Fig. 11



(*a*) (*b*)

Effect of temperature of deformation (wire-drawing) on the resistivity of (*a*) Ni and (*b*) Cu. ○ 100°C, +0°C, ● −78·5°C, □ −183°C.

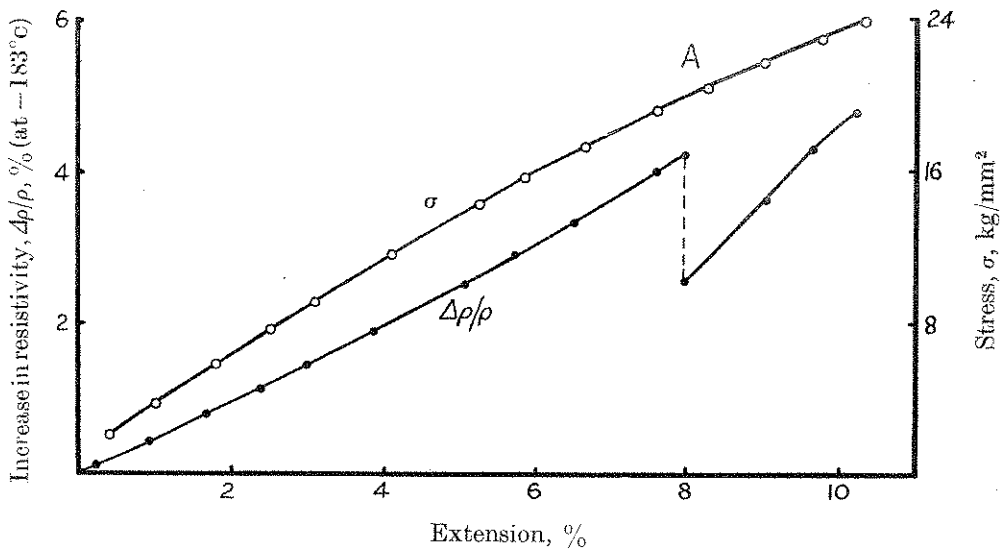
However, although there are some instances where the resistivity *increases* on annealing in certain temperature ranges it is convenient to continue to use the term ' recovery ' as this has come to have the general sense of change of a specified property on annealing.

The discovery (Druyvesteyn and Manintveld 1951) of low-temperature recovery after low-temperature deformation has stimulated considerable interest and greatly extended the temperature range in which recovery of resistivity can profitably be studied. In the following sections it will be convenient to discuss separately results obtained in three temperature ranges although it must be realized that the divisions are quite arbitrary (cf. § 5.3.5). A correlation of diverse recovery phenomena in pure metals will be attempted in § 6.1.

5.4.1. *' Low temperature ' Recovery*

Many recent developments in metal physics can be traced back to the experiments of Molenaar and Aarts (1950) in which they measured the change in resistivity and yield stress of wires of copper, silver and aluminium during extension at liquid air temperature. Their results for copper are shown in fig. 12. At the point A, extension at −183°c was discontinued and the speicmen brought to room temperature. After 10 min the specimen was re-cooled to −183°c and extension recommenced. It was found that the resistivity had fallen but that there had been no detectable change in yield stress. A similar result was found for silver, and more strikingly for aluminium where the decrease of the

Fig. 12



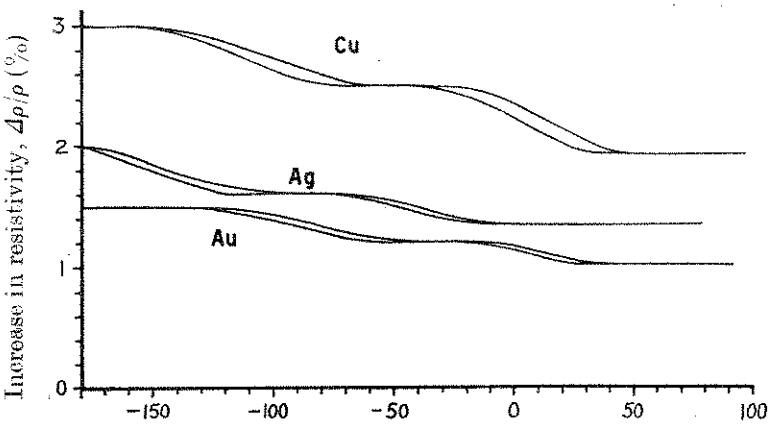
Resistivity changes and yield stress of Cu extended at −183°c. At point A there was an anneal of 3 hrs. at 20°c. (ρ_{-183} presumably about 0·29 $\mu\Omega$cm : Molenaar and Aarts 1950.)

resistivity due to deformation was much greater during the room temperature anneal. These experiments thus confirm earlier work (e.g. Tammann 1936) which indicated that some of the lattice defects responsible for the change in resistivity had a negligible effect on the yield stress. The recovery observed by Molenaar and Aarts has been investigated in detail by Druyvesteyn and Manintveld (1951) and by Manintveld (1952, 1953). The results shown in fig. 13 refer to resistance measurements at liquid air temperature following recovery times of 15 and 45 min at the temperatures indicated. It is clear that two discrete recovery processes are involved and by making the usual reaction rate theory assumptions, Manintveld found the values given in table 5 for the activation energies, Q_1,

which characterize the ' low temperature ' recovery, and those, Q_2, for the ' higher temperature ' recovery.

It was suggested that the mechanism of the second recovery step was due to the diffusion of single vacant sites and that the first was due to the diffusion of special aggregates of vacancies. Subsidiary calculations were made on the first of these assumptions and the specific suggestion that recovery takes place by the annihilation of vacancies at mosaic or grain boundaries. A diffusion formula was stated to agree with the results and an estimate of about one micron was given for an average mosaic block diameter in the copper and silver wires.

Fig. 13



Recovery data for wires extended at −183°c. Upper and lower curves for each metal refer to annealing times of 15 and 45 min respectively. $\Delta\rho/\rho$ measured at −183°c (Manintveld 1952).

Table 5. Recovery after Low-temperature Deformation

	Q_1 (ev)	Q_2 (ev)
Gold	0·29±0·03	0·69±0·06
Silver	0·18±0·02	0·69±0·07
Copper	0·20±0·03	0·88±0·09

Further work by Manintveld (1953) has been concerned with recovery after very heavy deformation at −183°c. Increases of resistivity of about 150% (at −183°c) were obtained by rolling copper wires in a special apparatus, and isothermal recovery experiments carried out. About one quarter of the increase in resistivity annealed out below −70°c with a unique activation energy of 0·25±0·02 ev ; recovery of another quarter took place in the range −70°c to 0°c, with a unique activation energy

of $0{\cdot}82 \pm 0{\cdot}04$ ev. Analysing the results as before, Manintveld found that the ' effective mosaic block diameter ' deduced from the rolling experiments was about one fiftieth of that deduced from the experiments in which wires were lightly deformed by stretching.

A limited number of resistance measurements on copper single crystals have been made by Blewitt *et al.* (1953) during experiments chiefly concerned with the influence of temperature on stress–strain curves. Pairs of single crystals of 99·999% purity were tested at −195° and 27°C. There were found no differences in critical shear stress or in rate of work hardening up to shear strains approaching 0·25. Resistance measurements were made on crystals deformed at −195°C both before and after one-hour anneals at 27°C. No recovery of resistivity was found after strains up to 0·25 but no evidence was given that the resistivity had been appreciably altered by the deformation (cf. § 5.2.1.1). Recovery was observed after strains greater than 0·25 and its magnitude increased with increasing prior strain. Sensitive stress–strain measurements following the annealing treatments showed that when recovery of resistivity occurred there was a slight *increase* in the stress for continued deformation and that characteristic yield point phenomena were obtained. Similar results have been obtained by Pry and Hennig (1953) using polycrystalline wires. Blewitt *et al.* conclude that appreciable deformation generates vacancies or other defects which raise the resistivity at −195°C but which can partially disappear on annealing at 27°C. Further, that some of these vacancies can ' anchor ' dislocations in a manner similar to that of carbon in iron (§ 5.2.2.2) and produce yield point phenomena (as predicted by Seitz 1952 a). By analogy with the work of Cottrell and Churchman (1949) on iron it is probable that part of the recovery of resistivity is associated with the strain-ageing process.

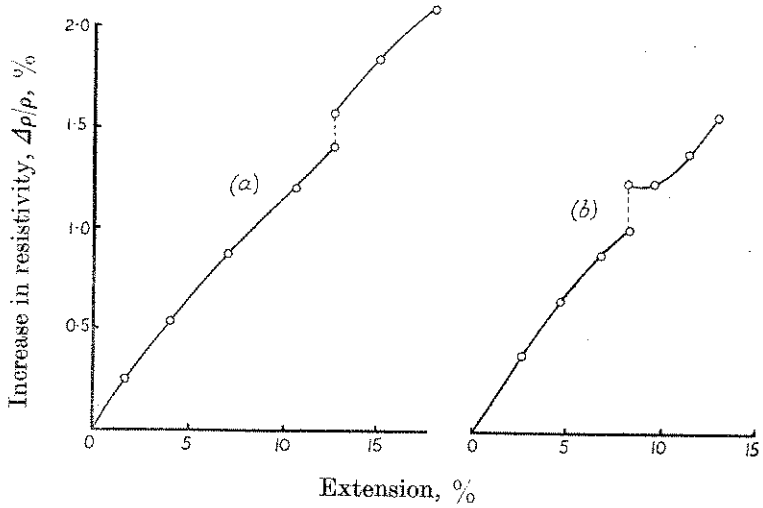
Preliminary results for recovery following deformation at very low temperatures have been given by Eggleston (1952). Annealed copper wires were twisted at 4·2°K to give an increase of resistivity of about $0{\cdot}1 \mu\Omega$cm. Isothermal recovery experiments at around −140°C did not give reproducible results unless a prior ' normalizing ' treatment of heating for 2 min at a temperature slightly higher than −140°C was first carried out. In the range −140° to 70°C recovery occurred with a deduced mean activation energy of $0{\cdot}44 \pm 0{\cdot}06$ ev. When this recovery process had been disposed of by heating for 2 min at a temperature slightly higher than −70°C, a second process was found to be operative just below room temperature. This had an apparent activation energy of $0{\cdot}67 \pm 0{\cdot}09$ ev.

The relationship between ' recoverable ' and ' unrecoverable ' resistivity for copper wires annealed at 13°C following deformation at −195°C has been studied by Pry and Hennig (1953). Their results are discussed in § 5.2.2.1.

Aarts and Jarvis (1953) have recently carried out preliminary work on recovery of resistivity of alloys after low-temperature deformation.

Two alloy systems were investigated: the first, copper–silver, being not altogether a satisfactory choice as it is eutectiferous with very little mutual solid solubility at room temperature. It is therefore likely that deformation results in precipitation phenomena which can have a marked effect on resistivity (§ 5.3.3). However, the recovery phenomena observed in copper–silver alloys were very similar to those found in pure metals. In the other system used, silver–gold (continuous solid solutions between the solidus and room temperature) striking results were obtained with two alloys. Annealing at room temperature following deformation at liquid air temperature caused an *increase* in the resistivity as shown in figs. 14 (*a*), (*b*). The reason for this ' anomalous recovery ' is not clear.

Fig. 14



Resistivity changes during extension of Ag–Au alloys at −183°c. Discontinuities due to room temperature anneals (cf. fig. 12) (*a*) 25/75 Ag/Au, $\rho_{-183}\simeq 6\,\mu\Omega$cm, (*b*) 50/50 Ag/Au, $\rho_{-183}\simeq 10\,\mu\Omega$cm (Aarts and Jarvis 1953).

Aarts and Jarvis have suggested it may be associated with the production, at low temperatures, of some kind of order which affects the resistivity; another suggestion made by Cottrell is discussed in § 6.3. Further experimental work is necessary to show whether the phenomenon is at all general in alloys.

5.4.2. ' *Normal Temperature* ' *Recovery*

In this present section it is intended to consider recovery measurements made at, or only slightly above the deformation temperature, where this was around room temperature. Recently Weyerer (1953) has shown that following extension of wires at room temperature, a temperature rise of only a few degrees can give marked recovery of resistivity. This was

particularly noticeable in pure copper as compared with copper of commercial purity and suggests that impurities are capable of ' trapping ' the defects (vacancies or interstitials) responsible for recovery at room temperature. A similar observation has been made by Brinkman *et al.* (1953). The results of Dugdale for deformed platinum heated at 70° and 90°C have been noted in § 3.2.1.

Room-temperature recovery of a rather spectacular magnitude has been reported by Linde (1950) for a gold–chromium alloy containing 22 atomic per cent chromium. The resistivity of this alloy *decreases* on deformation, but on ageing a heavily deformed wire at 20°C for 650 hours the resistivity increased by 4%. It was suggested that the decrease in resistivity on deformation might be due to a change in the electron-shell configuration of the chromium atoms and that the original state was slowly restored on ageing. (As similar results were obtained following quenching it is possible that the phenomena are associated with an order–disorder transformation in which the ordered structure has the higher resistivity, cf. Ni_3Cr, studied by Taylor and Hinton 1952.) Linde explained the *decrease* in resistivity on cold-working by reference to magnetic measurements on Au–Cr alloys which showed that cold-working caused a change in susceptibility in a sense corresponding to an increase of the average number of electrons in the d-shell of the chromium atoms. It was suggested that cold-work reduced the total capture of electrons by d-shells since certain atoms displaced from normal lattice positions obtained a more stable electronic configuration and their electrons no longer partook in the exchange between the shells and the electron gas. This effect may be sufficiently large to outweigh the increase in resistivity due to general lattice defects. Similar phenomena have been found in Au–Fe and certain ternary and quaternary alloys (Linde 1953).

Room temperature recovery in deformed β brass observed by Honeycombe and Boas (1948) is presumably to be attributed to re-ordering but it was much slower than that found by Eggleston after irradiation (§ 4.2.3).

The recovery of resistivity during the strain-ageing of iron studied by Cottrell and Churchman (1949) is of great interest, not only because it confirms Cottrell's theory of the yield point, but because it provides an estimate of the dislocation density in deformed iron wires (cf. § 5.1.2). The calculations of Bhatia (1949) showed that the transfer of carbon atoms from a random distribution in the iron lattice to atmospheres concentrated around dislocations will result in a decrease in resistivity. The recovery of resistivity due to this cause could be accounted for by using the activation energy for the diffusion of carbon atoms, but as nitrogen atoms would have a similar effect and a similar activation energy for movement, the identification of the atoms responsible is uncertain. A summary of Cottrell and Churchman's principal results is given in table 6.

Further work has been carried out by Lücke (1953, private communication) who has found by resistance measurements that dislocations in α-iron are capable of drawing in carbon atoms to the extent of about forty per atom plane.

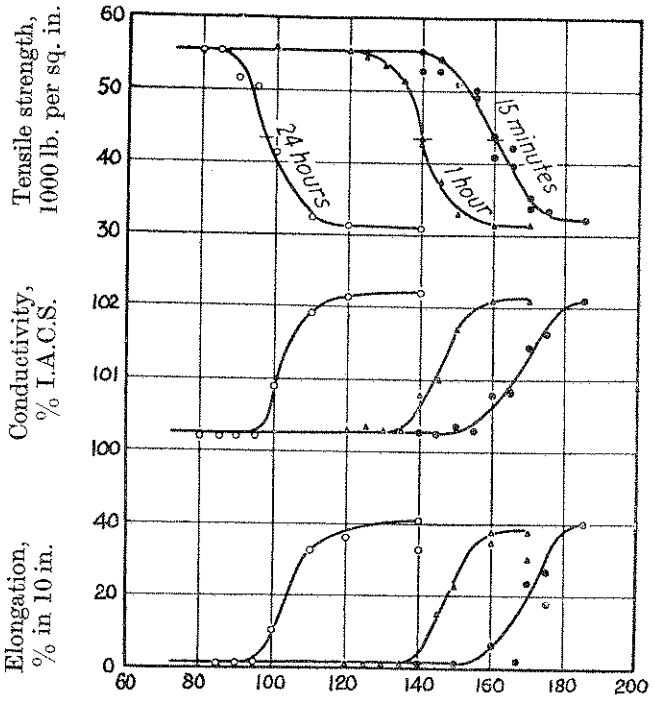
5.4.3. *'High Temperature' Recovery*

It is generally agreed that dislocations contribute to the resistivity due to deformation; in this section we shall therefore consider recovery effects which might reasonably be attributed to a reduction in dislocation

Table 6. Recovery during Strain-ageing of Iron at 31°C

Prior reduction by drawing %	Total change of resistance %	Estimated transfer of carbon %	Estimated dislocation density (lines/cm²)
8	0·18	0·0007–0·006	7×10^{10}–6×10^{11}
23	0·21	0·0008–0·007	8×10^{10}–7×10^{11}
42	0·24	0·0009–0·008	9×10^{10}–8×10^{11}

Fig. 15



Annealing characteristics of pure copper drawn 75%.
(102·3% I.A.C.S.≡1·67 $\mu\Omega$cm at 20°C: Smart, Smith and Phillips 1941.)

density. It is therefore of particular value to compare recovery of resistivity with recovery of other properties such as hardness and tensile strength which depend on dislocation density. Some results for high

purity copper (better than 99·999%) given by Smart, Smith and Phillips (1941) are shown in fig. 15. From their data it is possible to estimate the activation energy for recovery of the properties measured. In all cases (following reductions of 50, 75 and 87·5%) this was around 1·1 ev. On account of uncertain experimental errors it is difficult to know whether there were any real differences in activation energy but it is notable that in the range studied the temperature of ' half-recovery ' was always *greater* for resistivity than for tensile strength.

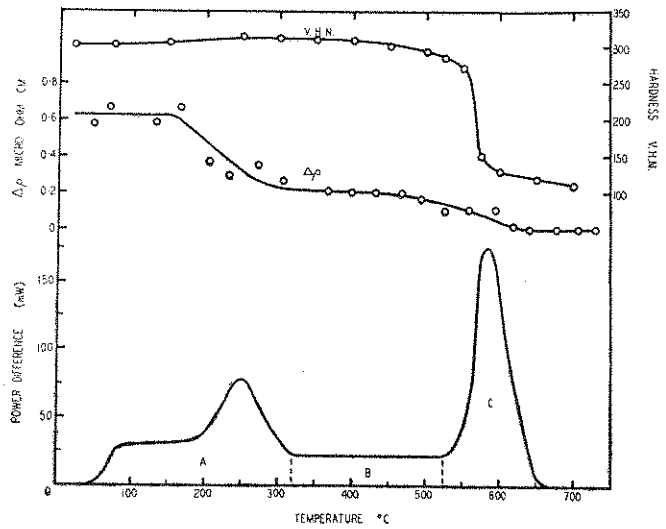
Bowen, Eggleston and Kropschot (1952) have also used copper (99·952%) in investigations of the response of the resistivity of hard-drawn wire (96·9% reduction) to pulse annealing at various temperatures. They claimed that their results indicate a unique activation energy of 1·23 ev for recovery in the range 100° to 250°C, but there was some indication that the energy was lower at the lower end of the temperature range. The suggestion of Mott (1952) that this recovery might have been due to the movement of interstitials is almost certainly incorrect in view of the similar and more extensive results of Smart *et al.* which show that dislocations must have been involved. Bowen *et al.* did analyse their results in terms of chemical reaction theory and concluded that a fourth order reaction was indicated. The activation energy estimated from this analysis was taken into account in giving the value of 1·25 ev. It is difficult to find a model to fit a fourth order reaction for recovery of resistivity and, for instance, it is by no means clear that the movement of dislocations, by glide or climb, can be described in terms of reaction theory.

A new analysis of the results of Bowen *et al.* has been made by Brinkman, Dixon and Meechan (1953). They assume, following Seitz (1952 a) that vacancies are able to impede the movement of dislocations so that removal of vacancies would result in some dislocation movements and changes in properties associated with dislocations. A specific model involving the disappearance of vacancies at grain boundaries and dislocations was then used and a good fit obtained with experimental data for the initial recovery period. The deduced activation energy assigned to vacancy migration was $1{\cdot}19 \pm 0{\cdot}01$ ev. There is obvious similarity between this model and that used by Manintveld (§ 5.4.1) with the assumption that vacancies move with an activation energy of about 0·8 ev. A detailed elaboration of both analyses would be desirable. The assignment of 1·19 ev to vacancy migration depends on delicate considerations more appropriately discussed in § 6.1 but it should be noted that this interpretation does depend on Seitz's suggestion and attempts to link vacancy recovery with recovery of mechanical properties. A connection might equally exist between interstitials and mechanical recovery. However, according to another view (Mott 1952, 1953) vacancies (or interstitials) can *aid* the movement of dislocations by attaching themselves to the extra half-planes and causing climb (or descent) from piled-up groups. Here there is a more intimate connection between defect diffusion and mechanical properties. One feature ignored by Brinkman *et al.* is the

possibility of long-range interaction between vacancies and dislocations for which a strain-ageing calculation would be appropriate (cf. Harper 1951).

The changes of various properties during recovery have been extensively studied by Tammann and his associates (for a general summary, see Tammann 1936). It was generally found that in copper, silver and gold the course of recovery of resistivity was similar to that of various mechanical properties, but in nickel, iron, platinum and palladium, recovery of resistivity commenced at a lower temperature than recovery of hardness. but not necessarily at a lower temperature than certain properties measured in a bend test. The generality of these findings is somewhat uncertain because of the influence which impurities are known to have on

Fig. 16



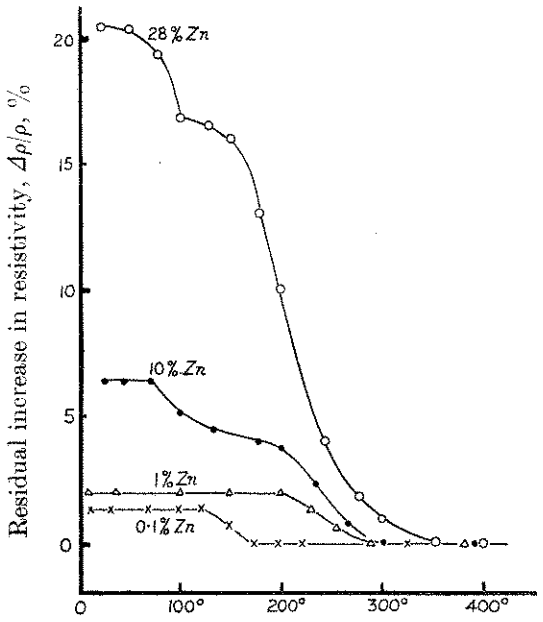
Recovery of cold-worked nickel (Clarebrough, Hargreaves and West 1953).

the properties of these metals as shown, for example, in experiments on platinum carried out by Middleton, Pfeil and Rhodes (1949). However, recent experiments of Clarebrough, Hargreaves and West (1953) have convincingly shown that recovery of resistivity in nickel takes place in two stages. the first of which being almost certainly the ' vacancy recovery ' found by Manintveld to occur in copper, silver and gold at around room temperature (§ 5.4.1). Measurements of resistivity, hardness and stored energy were made on similarly worked specimens with the results shown in fig. 16. It is clear that a considerable part of the increase in resistivity caused by deformation is attributable to vacancies (or to interstitials) which diffuse rapidly at about 200°c. The second recovery stage in nickel is due to a decrease in density of dislocations as shown by the

simultaneous changes in resistivity, hardness and stored energy. In similar experiments on pure copper deformed at room temperature only dislocation phenomena were observed.

Experiments by Tammann on recovery of resistivity in alloys showed that the single-stage recovery curves (isochronal anneals) typical of copper, silver and gold were frequently modified by increasing solute additions until eventually two apparently separate recovery processes occurred (fig. 17). This was found in alloys of copper with gold, manganese, tin and zinc ; alloys of silver with gold and zinc, but not in copper–nickel (up to 5% Ni). Hardness measurements were only made for an alloy of

Fig. 17



Recovery of resistivity of cold-rolled α brasses (97% reduction) for annealing times of ½ hr. (Tammann 1936).

copper with 28% Zn and for an alloy of silver with 23% Zn, but in both cases the hardness *increased* very slightly during the first drop in resistivity and finally fell at about the same temperature as the second drop in resistivity. Similar results have been reported for the resistivity and tensile strength of deformed 70/30 brass by Maddigan and Blank (1940) and for resistivity alone by Epifanov (1946).

It seems clear that the second (high temperature) process of recovery of resistivity and the change in mechanical properties are simply the result of a reduction in dislocation density, i.e. of recrystallization. The

mechanism of the first process is uncertain but there has been much speculation regarding the hardening frequently observed during the heating of deformed α brass below the recrystallization temperature. Masumotu, Saito and Sugihara (1952) have shown the existence of a specific heat anomaly at around 230°C in annealed α brass alloys of various zinc contents, and consider that their results support the hypothesis that the effects are due to the existence of short-range order below about 230°C. Other evidence for this has been put forward by Wilson (1939, pressure coefficient measurements) and by Guttman (1948, activity coefficient data). Thus an obvious interpretation of the recovery in resistivity at about 100°C shown in fig. 17 is that it is due to the re-establishment of local order disrupted by the prior deformation. There is however no direct evidence that local order has any large effect on resistivity (§ 6.3) and in particular there is no anomaly in resistance-temperature curves of annealed alloys at 230°C to correspond to the specific heat anomaly. Accordingly it is tentatively suggested that the recovery effects are due to the movement of vacancies or interstitials which can be present in high concentrations in some deformed alloys due to ' trapping ' by solute atoms (cf. the results of Clarebrough *et al.* for nickel, fig. 16). The 230°C temperature anomaly found by Masumotu *et al.* may be due to the dissociation of defect aggregates formed during the previous cooling, or to the generation of an equilibrium concentration (cf. §§ 3.1.1, 3.2.2). The increase in hardness could be due to strain-ageing caused by zinc atoms (Ardley and Cottrell 1953) or by vacancies.

It is finally necessary to refer to the numerous results which show that very high annealing temperatures sometimes result in an *increase* in resistivity (measured at room temperature) above a minimum value obtained by annealing at intermediate temperatures (see, e.g. Credner 1913, Takahasi 1930, Weyerer 1953). This has generally been thought to be due to the use of materials containing impurities which go into solution at high temperatures or to the solution of contaminants from the annealing environment. The extreme care necessary to produce a minimum resistivity in annealed copper has been emphasized by MacDonald and Pearson (1952); in very accurate work note must be taken of the quenching-in effects discussed in § 3.2, and also of a probable but very small effect of grain-size. However there is no convincing evidence that the resistivity of an annealed and pure metal is appreciably dependent on annealing temperature.

5.5. *Matthiessen's Rule*

This rule can be stated in several forms but perhaps the most useful is " the scattering of conduction electrons due to lattice vibrations is independent of that due to lattice defects when these are present in small concentration " (cf. Matthiessen 1862, Mott and Jones 1936). If this is so, we can express the observed resistivity, ρ, in the form

$$\rho = \rho_T(T) + \rho_0$$

where ρ_T is the resistivity due to lattice vibrations and is a function of temperature only, and ρ_0, the residual resistivity, is due to lattice defects and is temperature-independent. Therefore $d\rho/dT$ is a function of temperature only and is independent of the concentration of lattice defects, whether the defects are produced by quenching, by irradiation or by deformation. This expression of the rule immediately leads to another, namely, that the product of resistivity and temperature coefficient of resistivity is a function of temperature only. Thus, if we assume the validity of Matthiessen's Rule for a cold worked metal, determination of the change in temperature coefficient of resistance is equivalent to determining the change in resistivity and is not subject to errors arising from faulty measurement of specimen dimensions. Conversely, tests of the validity of Matthiessen's Rule must involve explicit determination of resistivity and be subject to the errors involved in such measurements. In particular, incorrect values of mean specimen cross-section due to the production by the deformation process of undetected internal flaws will lead to deviation from Matthiessen's Rule in the sense that $d\rho/dT$ is higher for deformed than annealed material. This we shall call a *positive* deviation. Positive deviations due to flaws or to structural inhomogeneity can probably be detected by annealing at such low temperatures that the flaws remain, and redetermining the value of $d\rho/dT$ for the annealed material. Results of experiments which show positive deviations from Matthiessen's Rule and have not been checked in this way are always suspect. Such deviations have in fact been reported by Berghout (1952) for silver between $-190°$ and 20°C and by Rutter and Reekie (1950) for pure copper and aluminium between $-250°$ and 20°C, but the deviations were small (change of $d\rho/dT$ by about 1% for a deformation of about 80%) and close to the probable experimental error. Bowen, Eggleston and Kropschot (1952) in their study of the annealing kinetics of drawn copper wires measured resistivities in the range 4·2° to 30°K and found Matthiessen's Rule accurately obeyed in the range 4·2° to 20°K. Above 20°K, deviations occurred in a positive sense. Similar results for irradiated copper have been found by Eggleston (private communication). Other workers have found no systematic deviations: the validity of Matthiessen's Rule (to within about 1%) has been shown by Geiss and van Liempt (1927) for deformed tungsten, molybdenum, nickel and platinum; by Masima and Sachs (1928 b) for deformed α brass single crystals; and by Lücke (1951) for hard-drawn commercial copper.

More accurate work with a statistical estimate of errors has been carried out by Boas and Nicholas (1953). They found that the rule is true to within 0·5% for nickel, copper (of two purities), iron and 80/20 brass, but not for 75/25 brass nor for an aluminium bronze. For wires of these alloys given a deformation corresponding to a logarithmic strain of 2·3 the deviations were such that $d\rho/dT$ was less than the value for annealed wires by about 1% in the case of 75/25 brass and by about 2%

for the aluminium bronze. Later and yet more accurate work by Clothier and Ogilvie (1953) has established that heavily cold-worked copper also gives negative deviations from Matthiessen's Rule amounting to about 0·3% decrease in $d\rho/dT$ for logarithmic strains of about 3.

Boas and Nicholas have given an interpretation of these deviations in terms of a change caused by deformation in the characteristic temperature, Θ, of a metal. They assume that the number of conduction electrons is not altered by deformation, and show that the fractional decrease in $d\rho/dT$ can be expressed as $2\delta\Theta/\Theta$. This change in Θ corresponds to an increase in the mean frequency of lattice vibrations and the interpretation would be confirmed if a detailed calculation showed that inhomogeneous distortions in a strained lattice do have this effect on lattice vibrations. Such a calculation has been attempted by Smoluchowski (1953).

A second explanation of deviations has been given by Klemens (1953). Rather than ascribing different thermal vibrations to atoms in distorted crystals, he proposes that the deviations are caused by a non-linear additivity of scattering probabilities of the conduction electrons. It is further assumed that atoms in the immediate neighbourhood of lattice imperfections are so far displaced from their mean positions that their thermal displacement contributions to resistivity become small. It is then possible to show that these assumptions can lead to results which are not inconsistent with both dislocation and stacking fault explanations of the resistivity due to deformation.

Theoretical work on the general validity of the Rule has been carried out by Sondheimer (1950).

5.6. *Anisotropy of Resistivity*

An early hypothesis put forward to account for the change in resistivity due to deformation suggested that the resistivity of annealed cubic crystals was anisotropic and that during the working of a polycrystalline aggregate the development of a preferred orientation led to a change in resistivity (Tammann 1914). This was finally rejected both on theoretical and on experimental grounds (Masima and Sachs 1928 a, Greenwood 1931, Fraser 1931) but although the resistivity of an annealed cubic metal is now known to be isotropic there is clear evidence that the resistivity of a cold-worked metal is sometimes not.

Anisotropy of resistivity may most simply be demonstrated in heavily cold-rolled strip although the effect is small. Statistical methods have been used (Broom 1951, 1952 a), to determine whether, in a given material, the resistivity in the longitudinal direction differed significantly from the resistivity in the transverse direction. Some typical results for rolled strip are given in table 7 together with results obtained using an elaborate technique for measuring anisotropy in cold-drawn wires (Broom and Clothier 1952). It will be seen that the longitudinal resistivity may be greater than, equal to, or smaller than the transverse resistivity.

There does not appear to be any way of accounting in detail for these differences, but according to all recent theories of the resistance due to dislocations (§ 2.1.3) any non-random array of dislocations will give rise to anisotropy of resistivity owing to anisotropy of scattering by the individual dislocations. Although theoretical work indicates the magnitude of scattering anisotropy, agreement with experiment can only be obtained by making arbitrary though plausible assumptions about the arrangement of dislocations.

Table 7. Anisotropy of Resistivity in Cold-worked Metals

Metal (alloy compositions in wt. %)	Resistivity at 20°C ($\mu\Omega$cm) (annealed)	Logarithmic strain	Fractional increase at 20°C %	
			Longitudinal	Transverse
Copper	1·68	2·9 (strip)	3·20 ±0·14	3·27 ±0·14
Nickel	9·94	2·9 (strip)	3·44 ±0·11	3·39 ±0·11
75/25 Copper–nickel	30·56	2·2 (strip)	3·34 ±0·16	4·03 ±0·16
70/30 Brass	6·17	2·9 (strip)	22·97 ±0·19	21·16 ±0·19
Copper	1·69	2·7 (wire)	2·3 ±0·2	2·9 ±0·2
80/20 Brass	5·47	1·96 (wire)	18·4 ±0·1	14·9 ±0·3
94/6 Aluminium bronze	11·13	1·96 (wire)	27·4 ±0·1	24·2 ±0·3

These difficulties can in part be overcome by measurements on thin strip lightly deformed in pure tension. It is possible to make assumptions about the arrangement of dislocations produced by cold-work and so make comparison with theory. This has been attempted by Berghout (1953) but experimental uncertainties were such that only general confirmation of theory was obtained.

While it is unlikely, owing to the complexity of deformation processes, that a quantitative treatment of anisotropy will be possible except for very special cases, it should be realized that anisotropy measurements provide evidence for the role of dislocations and stacking faults as compared with randomly dispersed vacancies or interstitials which scatter isotropically and would give no anisotropy of resistivity.

5.7. *Miscellaneous Observations*

The work reviewed so far in § 5 has been concerned with straightforward investigations of the effect of deformation and annealing upon the resistivity of metals. There are, however, some unusual experiments which merit attention because of their possible significance in relation to what has already been discussed.

5.7.1. *Anomalous Skin Resistance*

The high-frequency surface resistance of a metal is dependent, amongst other things, upon the d.c. resistivity of surface layers and upon surface roughness. At very low temperatures when the mean free path of the

conduction electrons becomes large compared to the thickness of the effective conducting layer, it is possible to compare experimental results with the theory of Reuter and Sondheimer (1949) and deduce values of the mean number of free electrons per atom. Chambers and Pippard (1953) have shown that unacceptable values are obtained if precautions are not taken to ensure that the d.c. resistivity of surface layers is the same as that of the interior of wires, which is measured and used in calculations. A series of experiments showed that light mechanical polishing of an annealed and electropolished copper wire resulted in the formation, at the surface, of a layer about 1 μ deep which had a d.c. resistivity about 5% higher (at 20°C) than that of the bulk material. This indicated the production and retention of a greater concentration of lattice defects than generally obtained by deforming bulk specimens (§ 5.3.1), and presumably demonstrates the complexity of the deformation caused by polishing. However, in accurate studies of annealing kinetics it is important to appreciate that the resistivity of worked wires may not be homogeneous, and that the recovery of surface layers may be particularly rapid. Such an effect has been pointed out by Bowen, Eggleston and Kropschot (1952).

5.7.2. *The Hall Effect*

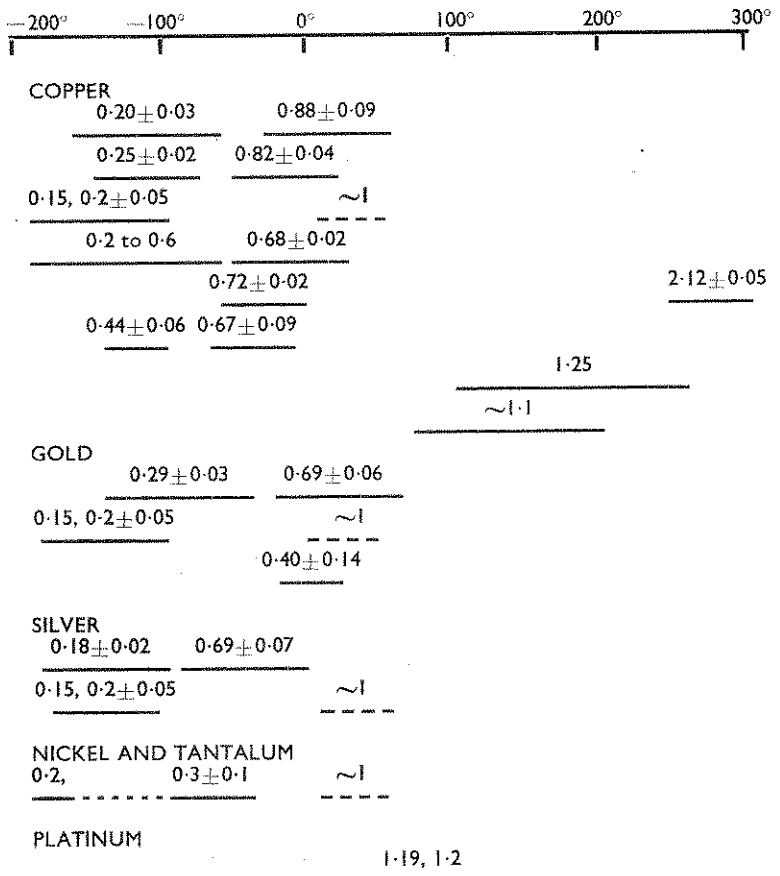
Wiener and Groetzinger (1952) have pointed out that determinations of the change of resistivity with deformation can be interpreted according to the free electron theory of metals, simply as providing information about changes in the product of the number of free electrons per unit volume with their mean free path. Because it is commonly assumed that changes in resistivity are due only to a reduction in mean free path, it is desirable to obtain an estimate of possible changes in free electron density. This can be done by determining the effect of deformation on the Hall constant since according to the free electron theory this constant is dependent only upon the number of free electrons per unit volume. Measurements on copper strip reduced 75% in cross section by cold rolling showed tht the Hall constant was decreased by about 1% by subsequent annealing, while the resistivity decreased by about 2·2%. The experiments were not of very high accuracy owing to the smallness of the effect and because their interpretation in terms of the idealized free electron theory is dubious, too much weight should not be given to the apparent indication of a change of free electron density due to cold-work. Further experimental work might profitably be carried out when a less naive theoretical treatment has been developed, using a material which gives a larger change in resistivity (such as α brass) and which may well give a larger change in Hall constant.

§ 6. General Discussion

6.1. *Activation Energies for Recovery*

A summary of determinations of activation energies for recovery of resistivity is given in fig. 18. The interpretation of those found for copper will now be examined in some detail. It has been generally

Fig. 18



Manintveld 1952, light deformation at —183°C.

Manintveld 1953, heavy deformation at —183°C.

Marx *et al.* 1952, deuteron bombardment at —140°C.

Overhauser 1953, deuteron bombardment at —180°C.

Eggleston 1953, α-particle bombardment at —150°C.

Eggleston 1952, heavy deformation at 4°K.

Bowen *et al.* 1952, heavy deformation at 20°C.

Smart *et al.* 1941, heavy deformation at 20°C.

Manintveld 1952, light deformation at —183°C.

Marx *et al.* 1952, deuteron bombardment at —140°C.

Kauffman and Koehler 1952, quenching from ~900°C to —195°C.

Manintveld 1952, light deformation at —183°C.

Marx *et al.* 1952, deuteron bombardment at —140°C.

Marx *et al.* 1952, deuteron bombardment at —140°C.

Dugdale 1952, deformation at 20°C and neutron bombardment at 40°C.

Observed activation energies for recovery of resistivity.

assumed that the well-defined process with activation energy 0·7 ev occurring at around −30°C is due to the movement of vacancies, mainly because of reasonable agreement with the well-established theoretical estimate of *c.* 1 ev for vacancy migration (§ 2.2.1). Overhauser (1953) was able to show that his data could be analysed in terms of a modified second-order reaction involving the annihilation of static interstitials by mobile vacancies. There is in fact some evidence from measurements of the shear modulus of copper wire deformed at −195°C that some interstitials can disappear during an annealing period of 15 min at ∼−75°C (Crittenden and Dieckamp 1953). It is important to establish whether recovery occurs by the movement of vacancies to interstitials or vice-versa. Brinkman, Dixon and Meechan (1953) in an extended discussion of the problem assign 0·7 ev to the migration of *interstitials*. They point out that equal numbers of vacancies and interstitials are produced in bombardment experiments, so that if 0·7 ev recovery is predominantly due to annihilation of pairs, there will be very few of the immobile defects left to migrate and disappear at higher temperatures. No well-defined recovery process in bombarded copper has been observed between 0° and 200°C (Overhauser 1953, Eggleston 1953). On the other hand, deformation is thought to produce more vacancies than interstitials (§ 5.1.1) so that any well-defined recovery process above 0°C should be due to vacancies if they were immobile during the 0·7 ev recovery at ∼−30°C. In deformed copper the situation is confused by the presence of dislocations, but Brinkman *et al.* do claim to have disentangled an activation energy of 1·19 ev from the early stages of the 100° to 250°C recovery of Bowen *et al.* (§ 5.4.3). This they assign to vacancy migration. It seems simpler to regard the recovery observed above 100°C as due to dislocations only and to conclude that the 0·7 ev process is due to the movement of vacancies. After deformation, a fraction of the vacancy concentration would serve to annihilate all interstitials and the rest could disappear by some of the mechanisms discussed below. However, Brinkman *et al.* find some support for their assignment from their interpretation of experiments on Cu_3Au (criticized in § 4.2.3) and from Nowick's data on quenched silver–zinc alloys (§ 3.2.2). Although there is little conclusive evidence there seems no compelling reason for ceasing to associate 0·7 ev recovery with the movement of vacancies.

With regard to the value of the activation energy there is a discrepancy between the 0·82 ev of Manintveld and other values clustered around 0·7 ev. Overhauser has shown that diffusion of vacancies may be modified by the presence of strains caused by a comparable concentration of interstitials (in irradiation experiments) and it is possible that Manintveld's results refer to defect movement in a less-strained lattice. Alternatively the difference may simply be due to experimental error or to differences in purity of the copper used.

Overhauser's vacancy-interstitial annihilation kinetics which fit the 0·7 ev recovery refer to defects which start to move when out of range

Observed activation energies for recovery of resistivity.

of each other's influence. Close vacancy–interstitial pairs such as are likely to be produced in irradiation experiments will move together more or less readily depending on their initial separation. This conception readily explains the range of activation energies found during recovery between −185° and −60°C after irradiation. In contrast, the recovery between −160° and −60°C reported by Manintveld after deformation at −183°C has a unique activation energy of 0·25 ev. The only process so far treated theoretically which might account for this is vacancy pair migration (§ 2.2.1). We know little about the likelihood of the production of grouped defects by low-temperature deformation (§ 5.1.1) and it is possible that the 0·25 ev recovery corresponds to a rearrangement of a complex defect. The 0·44 ev recovery reported by Eggleston (1952) may have been due to simultaneous 0·25 and 0·7 ev recovery.

Reduction in dislocation density is almost certainly associated with the recovery data obtained between 80° and 250°C after room-temperature deformation (§ 5.4.3). Therefore the exact activation energies have little significance, except in so far as it may be possible to extract an activation energy for movement of deformation-produced vacancies or interstitials if either are associated with dislocation movements (Brinkman *et al.*1953). After irradiation, Eggleston (1953) has found an apparently unique recovery process in the range 250° to 300°C and points out that the observed activation energy, 2·12 ev, is very close to that for self-diffusion in copper. Many recovery processes which would involve the creation and diffusion of vacancies can be imagined, examples being the disappearance of voids or sessile dislocations previously formed in thermal spike regions or by aggregation of vacancies.

The recovery data for Au, Ag, Ni, Ta and Pt can be related to the previously discussed results for Cu, bearing in mind that a given process will have a higher activation energy in metals of higher melting point (i.e. Ni, Ta and Pt). The only unusual result is that of 0·4 ev for recovery in Au after quenching. This is a preliminary result and its doubtful significance has already been discussed in § 3.2.1.

It will be appreciated that considerable weight attaches to the observation of unique activation energies and when recovery experiments are carried out, every effort should be made to establish that experimental arrangements are not modifying results and that reaction rate theory is applicable. For example, when studying the precipitation of carbon and nitrogen in α iron, Wert (1949) found that consistent activation energies were not obtained unless a pre-precipitation treatment was given to create nuclei to which subsequent diffusion could occur. Similarly, in resistivity studies on copper deformed by torsion at 4°K, Eggleston (1952) found that he could not get reproducible recovery unless some form of 'stabilizing' treatment was given.

Although measurements of resistivity have yielded much useful information it should be emphasized that ambiguities in interpretation will more readily be resolved when other techniques of investigation are

simultaneously employed. Of these the most important are likely to be the measurement of stored energy and elastic constants. For example Dienes (1953) has shown that interstitials increase the elastic moduli considerably while vacancies cause a less considerable decrease for an equivalent given concentration. Tammann (1936) found that the elastic modulus of nickel decreases considerably during the first recovery step (cf. fig. 16) so that this almost certainly involves removal of interstitials as well as the vacancies considered by Clarebrough *et al.* (1953) to have been the major source of the corresponding stored-energy change.

6.2. *Recovery Mechanisms*

Recovery due to annihilation of close vacancy-interstitial pairs is too simple and that due to reductions in dislocation density is too complex to warrant further discussion from the viewpoint of possible mechanisms. Four separate possibilities have been suggested to account for recovery due to the diffusion of single vacancies. First, vacancies can disappear on combination with interstitial ions : Nabarro (1948) has shown that such annihilations will be responsible for most of the removal of vacancies when the initial concentration of both vacancies and interstitial ions is high. e.g. under intense neutron bombardment (cf. Brown, Fletcher and Machlup 1953). Although Overhauser (1953) has discussed such a process in explaining his results, detailed kinetics do not appear to have been worked out. When the concentration is low, a second mechanism becomes more prominent, namely disappearance of vacancies at mosaic or grain boundaries (Nabarro 1948). Such a mechanism has been invoked by Manintveld (1952) to account for recovery after low-temperature deformation and good agreement was obtained between experiment and detailed kinetics involving diffusion data. Reasonable orders of magnitude for mosaic size were obtained, $1\,\mu$ for copper wire slightly extended and $0{\cdot}02\,\mu$ for wire heavily cold-rolled. A third possible process, so far not treated analytically, is the interaction between vacancies and dislocations. It is clear that vacancies will be attracted to the edge of the extra half-plane of an edge dislocation, but it is unlikely that any *single* vacancy can ' add on ' (i.e. be absorbed) and cause climb of the dislocation out of its original slip plane (Nabarro 1948). There are however the possibilities that a line of vacancies can accumulate and cause climb and that addition of single vacancies can occur at special sites such as jogs ; the dissociation of dislocations in face-centred cubic metals obviously makes these possibilities less plausible. Some attachment of vacancies to dislocations reminiscent of strain-ageing in iron can apparently occur as shown by the experiments of Blewitt, Redman and Sherrill (1953) on copper single crystals. Yield-point phenomena developed at the same time as recovery in resistivity took place (§ 5.4.1). Fourth, and last, there is the possibility of combination of vacancies to form pairs or larger groups. An initial obstacle to the latter suggestion is that vacancy pairs are relatively so very mobile that the attachment

of further vacancies would seem very unlikely before annihilation of the pair occurred at a boundary. However, once some groups had been nucleated such a process becomes plausible. Blin and Guinier (1951) claim to have shown, by x-ray diffraction, the presence of 6 Å diameter *cavités* in cold-worked copper, but it is possible that such voids are a direct result of the working process. Although Seitz (1952 a) has suggested many mechanisms for the production of vacancies by moving dislocations it is not clear that effective dispersal will occur when geometrical considerations call for contiguous creation of large numbers of vacancies (Mott 1953, private communication). Thus relatively large holes may be created and constitute either the *cavités* of Blin and Guinier or the nuclei for subsequent precipitation of single vacancies during recovery. An important special case of agglomeration of holes is the formation of a disc-shaped aggregate which when sufficiently large can collapse to give a stacking fault surrounded by a sessile dislocation. This process may be responsible for some of the persistent resistivity increases which in various experiments have been difficult to anneal out and about which comparatively little is known.

It now remains to consider a process by which vacancies can be prevented from moving and taking part in any of the recovery mechanisms mentioned. According to the results of Weyerer (1953) the purity of cold-worked copper has a marked effect on recovery of resistivity at around room temperature, and it was earlier suggested (§ 5.4.3) that this might be due to the trapping of vacancies by solute atoms. If this can occur in relatively pure metals it might account for some variations observed in resistivity studies. There is certainly an effect in less dilute alloys if the development of a second recovery stage with increasing solute concentration (fig. 17) is due to vacancies.

This discussion of recovery mechanisms has been primarily concerned with processes depending on the diffusion of vacancies. Interstitials have not generally been considered in this way but it will be clear that they can undergo the same types of interactions as those described for vacancies, i.e. with mosaic boundaries, with dislocations, with each other and with solute atoms.

6.3. *The Resistivity of Non-Random Alloys*

The major problems concerning effects of various lattice defects on the resistivity of pure metals have been reviewed in §§ 6.1 and 6.2. In alloys a new type of problem arises because the introduction of lattice defects may upset some form of atomic segregation previously present or may cause segregation where none previously existed. Familiar examples are the disruption of long-range order by cold-work and the strain-ageing of iron. The accompanying resistivity changes are reasonably well understood and do not merit discussion here. Some resistance changes caused by the introduction of defects into certain alloys have not been readily explicable in terms of effects found in pure metals or in alloys known to possess long-range order.

First, it has already been noted in § 5.3.2 that with two exceptions, single phase alloys give higher increases in resistivity, $\Delta\rho$, for a given deformation than the appropriate pure solvent metal. Many alloys give high relative increases, $\Delta\rho/\rho$. This behaviour has frequently been ascribed to the destruction of short-range order which it is assumed is present in the annealed alloys and is responsible for a lower original resistivity than would be given by a random alloy. Although there is some evidence that short-range order may be present in some alloys which give large increases in resistivity (cf. § 5.4.3) it has also been found that a small relative increase in resistivity is given by a 50/50 silver–gold alloy which possesses short-range order. However, such arguments are unconvincing because direct observation of the effective destruction of short-range order has not been made. Many x-ray investigations have demonstrated varying short-range order in Cu_3Au above the critical temperature for long-range order (e.g. Cowley 1950) but other experiments have revealed no anomalous resistivity changes with temperature above the critical temperature (Sykes and Evans 1936). If short-range order can be effectively quenched-in, then the data of Clarebrough and Nicholas (1950) on Ag_3Mg and of Brinkman *et al.* (1953) on Cu_3Au disclose no effect of short-range order on the resistivity of alloys quenched from various temperatures above the critical temperature. Again, if as an approximation, short-range order is regarded as long-range order with very small domain size there is both theoretical and experimental evidence (Jones and Sykes 1938) that the resistivity of Cu_3Au with small domains is very close to that of a random alloy. Recent theoretical work by Murakami (1953) has predicted a considerable effect of short-range order on the resistivity of a simple cubic AB lattice but his results seem to bear no relation to changes in resistivity of alloys known to possess short-range order above the critical temperature for long-range order. Much more evidence is needed on a possible effect of short-range order on resistivity but at present it must be concluded that the effect, if it exists, is very small.

Second, it is necessary to mention other types of atomic segregation which may be affected by lattice defects. Walker, Blin and Guinier (1952) have shown that ' clustering ' of zinc atoms occurs in aluminium–zinc alloys in the single-phase region. The effects of such clusters on resistivity are not known (except by possible analogy with the behaviour of age-hardening alloys) but it is probable that lattice defects in an alloy containing clusters would give abnormal resistivity changes. This hypothesis has been put forward to account for unusual resistivity changes in certain alloys (e.g. Ni_3Cr, Lücke 1953, private communication) but anomalous ordering behaviour offers a more plausible explanation (Taylor and Hinton 1952, § 5.4.2).

Finally, Cottrell (1953 c) has pointed out the possibilities of segregation in solid solutions due to the interactions of solute atoms with dislocations. From the viewpoint of resistivity changes, one of the most interesting arises from a prediction of Suzuki (1952) that solute atoms will attempt

to segregate in the stacking faults associated with dissociated dislocations in f.c.c. metals. Cottrell has shown that if this occurs the stacking fault should widen and has suggested that this may account for the increases in resistivity observed on annealing some silver–gold alloys at room temperature after low-temperature deformation (cf. fig. 14, Aarts and Jarvis 1953).

ACKNOWLEDGMENTS

I should like to thank Mr. J. F. Nicholas, Professor A. H. Cottrell, Professor M. J. Druyvesteyn, Dr. S. C. Hunter and Mr. R. A. Dugdale for helpful comments on the first draft of this article. I am also indebted to many who have supplied me with results and manuscripts prior to publication and who have generously given permission to quote from them. Acknowledgement of permission to reproduce diagrams and figures is made to *Acta Metallurgica* (fig. 9); the Physical Society (fig. 11); the Editors of *Nature* (fig. 13); the American Institute of Mining and Metallurgy (fig. 15); *Philosophical Magazine* (fig. 16); and the authors concerned.

Note added in proof.—A new calculation by H. B. Huntington (1953, *Phys. Rev.*, **91,** 1092) of the activation energy for movement of interstitial atoms in copper gives a value of ~0·25 ev. Huntington accordingly attributes annealing in copper at ~—100°C (fig. 18) to migration of interstitials, and that at ~—30°C to single vacancies. This seems to provide a very satisfactory resolution of many ambiguities in interpretation (§§ 6.1, 6.2) although it necessitates a critical reassessment of the annihilation kinetics discussed by Overhauser (1953).

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